Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Photoredox-catalyzed Redox-Neutral Difluoroalkylation to Construct Perfluoroketone with Difluoroenoxysilanes

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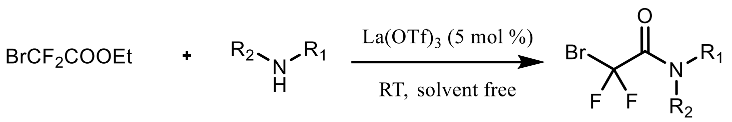
Table of Contents

1. General information

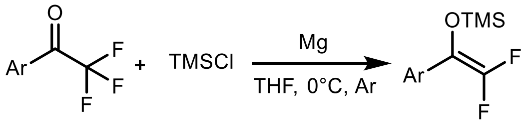
Analytical TLC was performed with silica gel GF254 plates. A 200-300 mesh silica gel was used for column chromatography. Solvents were distilled prior to use and were not deaerated before we used. All chemicals were used as received from commercial resources without further purification unless otherwise stated. ^{1}H NMR spectra were recorded on Bruker AVANCE III 400 and INOVA instruments with 400 and 600 MHz frequencies, and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 and INOVA instruments with 400 and 600 MHz with 101 and 151 MHz frequencies. ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer with a ^{19}F operating frequency of 376 MHz. The chemical shifts in ^{1}H NMR spectra were determined with Si $(CH_3)_4$ as the internal standard (δ = 0.00 ppm); the chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.0 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, m = multiplet, dt = triplet of doublets. HR-MS was obtained using a Q-TOF instrument equipped with an ESI source.

2. General procedure for the synthesis of 1a – 1h



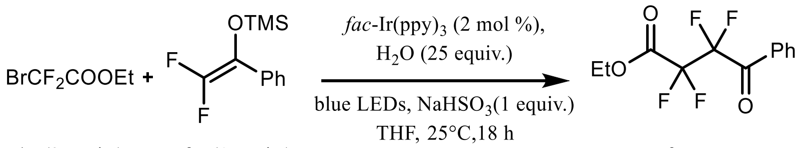
Compound **1** was prepared according to the literature.[1] A 10 mL reaction tube equipped with a magnetic stir bar was added with catalyst $La(OTf)_3$ (0.5 mmol, 5 mol %). Then the tube was pump and refilled with the Ar three times. The $BrCF_2COOEt$ (12 mmol, 1.2 equiv.) and amine (10 mmol, 1 equiv.) was added. The reaction was stirred at room temperature until the amine was exhausted. The reaction was purified by silica gel column chromatography to afford the products (**1a-1h**).

3. General procedure for the synthesis of 2a – 2o



Compound **2** was prepared according to the literature.[2] To a three-necked 50 mL round-bottomed flask equipped with a magnetic stir bar was added Mg (40 mmol, 4 equiv.). The flask was pump and refilled with Ar three times and TMSCl (40 mmol, 4 equiv.) and THF (25 mL) were added. Then the reaction was cooled to 0°C and trifluoroacetophenone (10 mmol, 1 equiv.) was added dropwise for almost 10 min. The reaction was stirred for 30 min at 0°C. After evaporation of solvent, the residue was added hexane (50 mL) and filtered. The filtrate was concentrated to afford the products without additional purification (**2a-2o**).

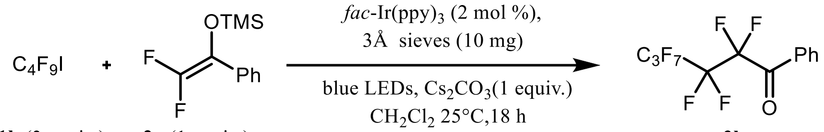
4. Typical procedure for the synthesis of 3aa – 3ja, 3ab – 3an



1a (3 equiv.) **2a** (1 equiv.) **3aa**

An over-dried Schlenk tube equipped with a magnetic stir bar was added with *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol %) and $NaHSO_3$ (0.2 mmol, 1 equiv.). The tube was evacuated and backfilled with argon for three times. A solution of $BrCF_2COOEt$ (0.6 mmol, 3 equiv.), H_2O (5 mmol, 25 equiv.) and difluoroenoxysilane (0.2 mmol, 1 equiv.) in anhydrous THF (2 mL) was added via syringe. The reaction was stirred at room temperature for 18 h under the blue LEDs irradiation ($\lambda = 450 \pm 15$ nm, 3 W electrical power, 3cm away). After the reaction, the residue was concentrated and purified by flash chromatography on silica gel to afford the corresponding product **3aa**.

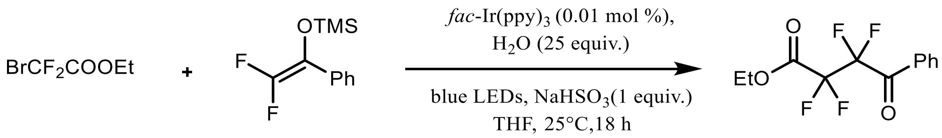
5. Typical procedure for the synthesis of 3ka – 3la



1k (3 equiv.) **2a** (1 equiv.) **3ka**

An over-dried Schlenk tube equipped with a magnetic stir bar was added with *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol %), 3 Å sieve (10 mg) and Cs_2CO_3 (0.2 mmol, 1 equiv.). The tube was evacuated and backfilled with argon for three times. A solution of C_4F_9I (0.6 mmol, 3 equiv.), and difluoroenoxysilane (0.2 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (2 mL) was added via syringe. The reaction was stirred at room temperature for 18 h under the blue LEDs irradiation ($\lambda = 450 \pm 15$ nm, 3 W electrical power, 3cm away). After the reaction, the residue was concentrated and purified by flash chromatography on silica gel to afford the corresponding product **3aa**.

6. Typical procedure for gram-scale synthesis with 0.01 mol % catalyst loading

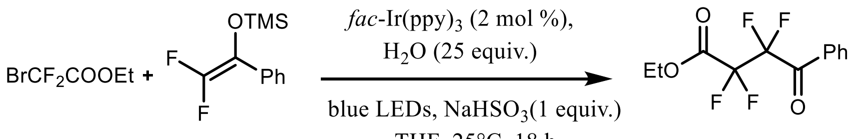


1a (3 equiv.) **2a** 1.14g(1 equiv.) **3aa** 1.04g

A 100 mL round bottom flask equipped with a magnetic stir bar was added with $NaHSO_3$ (5 mmol, 1 equiv.). The round bottom flask was evacuated and backfilled with argon for three times. A solution of $BrCF_2COOEt$ (15 mmol, 3 equiv.), H_2O (125 mmol, 25 equiv.) difluoroenoxysilane (5 mmol, 1 equiv.) and *fac*-Ir(ppy)$_3$ (0.0005 mmol, 0.01 mol %) in anhydrous THF (50 mL) was added via syringe. The reaction was stirred at room temperature for 18 h under the blue LEDs irradiation ($\lambda = 450 \pm 15$ nm, 3 W electrical power, 3cm away). After the reaction, the residue was concentrated and purified by flash chromatography on silica gel to afford the corresponding product **3aa**.

7. Condition Optimization for Difluoroalkylation

Table S1. Screen of ratio for difluoroalkylation



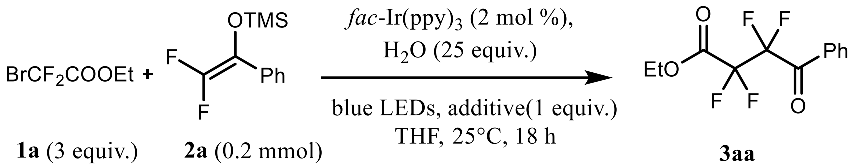
1a (x equiv.) **2a** (0.2 mmol) **3aa**

entry	**1a** (x equiv.)	**3aa** (%) [a]
1	1	50
2	1.5	67

3	2	75
4	2.5	80
5	3	85

[a]Reaction conditions: **1a** (x equiv.), **2a** (0.2 mmol), *fac*-Ir(ppy)$_3$ (2 mol %), $NaHSO_3$ (1 equiv.), H_2O (25 equiv.) THF (2 mL), irradiation with visible light under an Ar atmosphere at room temperature, 18 h. Yields determined by ^{19}F NMR using Benzotrifluoride as an internal standard.

Table S2. Screen of additive for difluoroalkylation

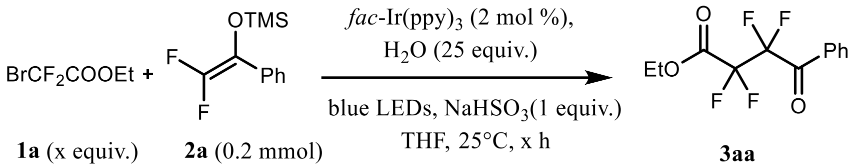


1a (3 equiv.) **2a** (0.2 mmol) **3aa**

entry	additive	3aa (%) [a]
1	$NaHSO_3$	83
2	K_2CO_3	45
3	Cs_2CO_3	50
4	$NaHCO_3$	51
5	KOAc	49

[a]Reaction conditions: **1a** (3 equiv.), **2a** (0.2 mmol), *fac*-Ir(ppy)$_3$ (2 mol %), additive (1 equiv.), H_2O (25 equiv.) THF (2 mL), irradiation with visible light under an Ar atmosphere at room temperature, 18 h. Yields determined by ^{19}F NMR using Benzotrifluoride as an internal standard.

Table S3. Screen of reaction time for difluoroalkylation

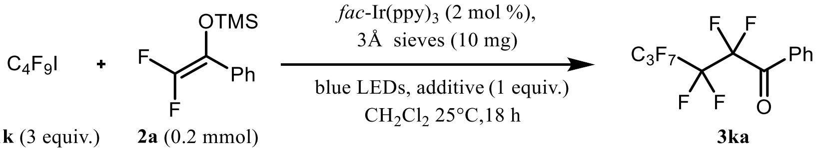


1a (x equiv.) **2a** (0.2 mmol) **3aa**

entry	Time (x h)	3aa (%) [a]
1	12	70
2	18	85
3	24	81
4	36	83

[a]Reaction conditions: **1a** (3 equiv.), **2a** (0.2 mmol), *fac*-Ir(ppy)$_3$ (2 mol %), $NaHSO_3$ (1 equiv.), H_2O (25 equiv.) THF (2 mL), irradiation with visible light under an Ar atmosphere at room temperature, x h. Yields determined by ^{19}F NMR using Benzotrifluoride as an internal standard.

Table S4. Screen of reaction time for perfluoroalkylation



entry	Additive	3ka (%) [a]
1	Cs_2CO_3	75
2	Na_2CO_3	44
3	$NaHCO_3$	24
4	K_3PO_4	55

aReaction conditions: **1k** (3 equiv.), **2a** (0.2 mmol), *fac*-Ir(ppy)$_3$ (2 mol %), additive (1 equiv.), 3 Å sieve (10 mg), CH_2Cl_2 (2 mL), irradiation with visible light under an Ar atmosphere at room temperature, 18 h. Yields determined by ^{19}F NMR using Benzotrifluoride as an internal standard.

8. Typical reaction set up

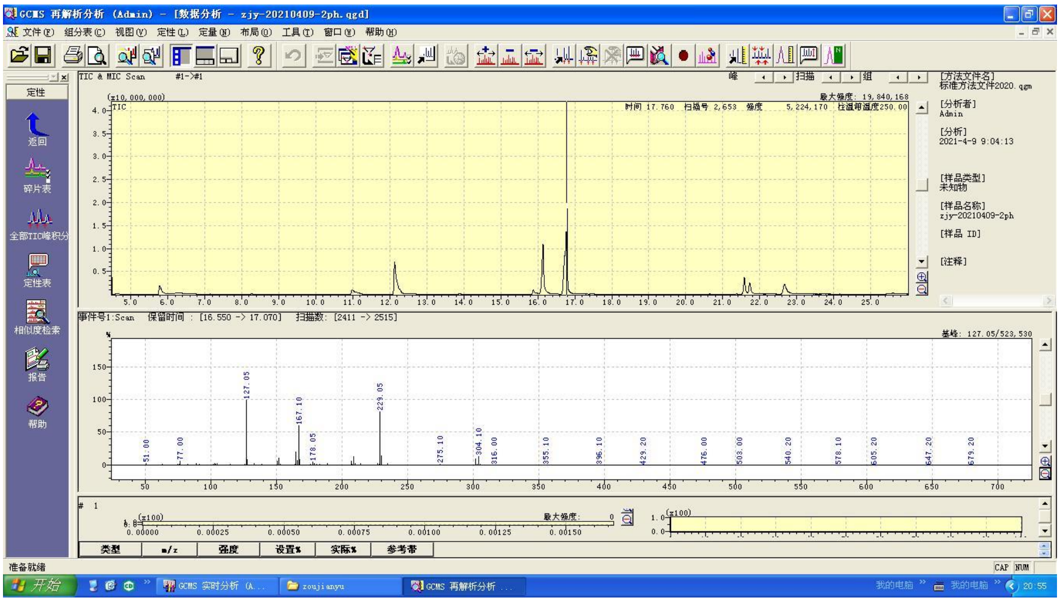
9. Mechanism studies

9.1 TEMPO Trapping Experiment

An over-dried Schlenk tube equipped with a magnetic stir bar was added with *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol %), TEMPO (0.6 mmol, 3 equiv.) and $NaHSO_3$ (0.2 mmol, 1 equiv.). The tube was evacuated and backfilled with argon for three times. A solution of $BrCF_2COOEt$ (0.6 mmol, 3 equiv.), H_2O (5 mmol, 25 equiv.) and difluoroenoxysilane (0.2 mmol, 1 equiv.) in anhydrous THF (2 mL) was added via syringe. The reaction was stirred at room temperature for 18 h under the blue LEDs irradiation ($\lambda = 450 \pm 15$ nm, 3 W electrical power, 3cm away). After the reaction, the residue was concentrated and purified by flash chromatography on silica gel to afford the corresponding trapping product **4** with 47% yield and **3aa** with trace yield.

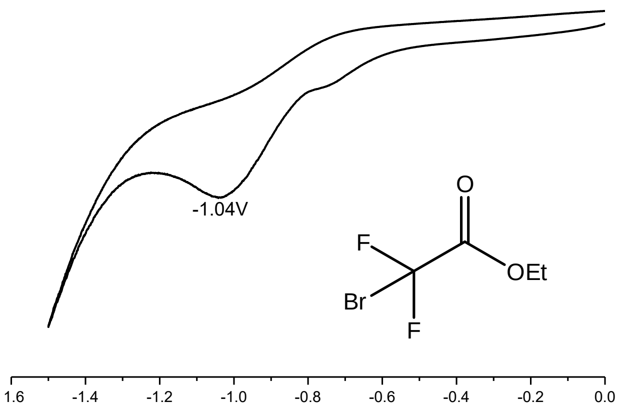
9.2 1,1-diphenylethyene Trapping Experiment

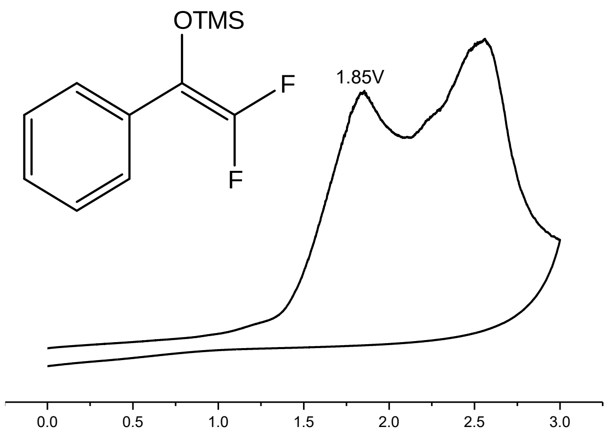
An over-dried Schlenk tube equipped with a magnetic stir bar was added with *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol %), 1,1-diphenylethyene (0.6 mmol, 3 equiv.) and $NaHSO_3$ (0.2 mmol, 1 equiv.). The tube was evacuated and backfilled with argon for three times. A solution of $BrCF_2COOEt$ (0.6 mmol, 3 equiv.), H_2O (5 mmol, 25 equiv.) and difluoroenoxysilane (0.2 mmol, 1 equiv.) in anhydrous THF (2 mL) was added via syringe. The reaction was stirred at room temperature for 18 h under the blue LEDs irradiation ($\lambda = 450 \pm 15$ nm, 3 W electrical power, 3cm away). After the reaction, the residue was concentrated and filtered. The corresponding trapping product **5** was detected by GC-MS.

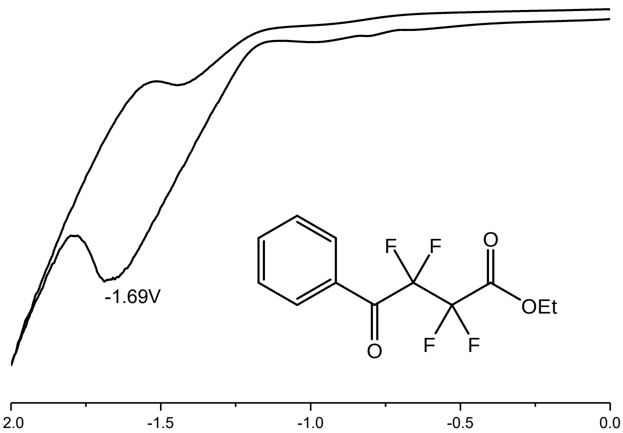


9.3 CV experiments for reagents and product 3aa

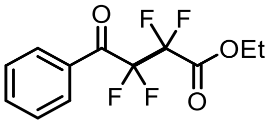
Cyclic voltammogram $BrCF_2COOEt$, difluoroenoxysilane and **3aa** in 0.1 M TBAP/MeCN at a glassy carbon working electrode with a Pt counter electrode and saturated calomel electrode (SCE). Potential sweep rate was 50 mV/s.



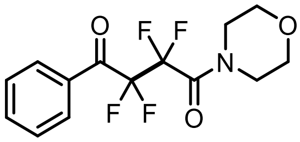

OTMS
F
F
1.85V
0.0
0.5
1.0
1.5
2.0
2.5
3.0


-1.69V
F
F
O
O
OEt
F
F
2.0
-1.5
-1.0
-0.5
0.0

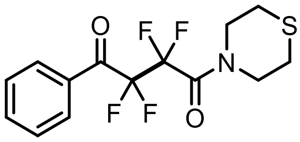
10. Compounds characterization



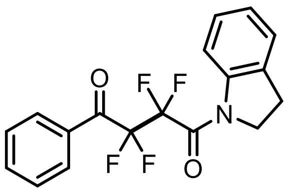
Ethyl 2,2,3,3-tetrafluoro-4-oxo-4-phenylbutanoate (3aa)[3]: colorless oil (45.6 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.4 Hz, 2H), 7.73 – 7.69 (m, 1H), 7.57 – 7.53 (m, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4 (t, *J* = 27.0 Hz), 159.8 (t, *J* = 29.0 Hz), 135.5, 130.9, 130.2 (t, *J* = 3.0 Hz), 129.0, 113.7 (t, *J* = 28.0 Hz), 111.3 – 110.4(m), 108.6 – 107.8 (m), 105.4 (t, *J* = 28.0 Hz), 63.9, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.13 (t, *J* = 4.4 Hz), -120.48 (t, *J* = 5.1 Hz); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{12}H_{10}F_4O_3Na$, 301.0458; Found, 301.0459.



2,2,3,3-tetrafluoro-1-morpholino-4-phenylbutane-1,4-dione (3ba): colorless oil (33.5 mg, 49% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.63 (m, 1H), 7.52 – 7.50 (m, 2H), 3.77 (s, 4H), 3.75 – 3.73 (m, 2H), 3.63 – 3.62 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.1 (t, *J* = 26.8 Hz), 158.5 (t, *J* = 25.6 Hz), 134.4, 132.3, 129.9 (t, *J* = 3.3 Hz), 128.7, 113.7 (t, *J* = 26.7 Hz), 112.7 – 111.7 (m), 110.9 – 109.9 (m), 109.0 (t, *J* = 24.6 Hz), 66.5 (d, *J* = 13.7 Hz), 46.1 (t, *J* = 5.5 Hz), 43.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.65 – -111.67 (m, 2F), -114.88 – -114.90 (m, 2F); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd. for $C_{14}H_{13}F_4NO_3Na$, 342.0724; Found, 342.0722.

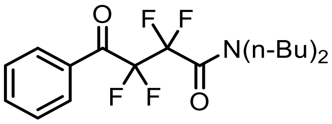


2,2,3,3-tetrafluoro-1-phenyl-4-thiomorpholinobutane-1,4-dione (3ca): colorless oil (30.6 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.01 – 3.95 (m, 2H), 3.87 – 3.81 (m, 2H), 2.76 – 2.71 (m, 2H), 2.68 – 2.62 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.2 (t, *J* = 26.7 Hz), 158.6 (t, *J* = 25.6 Hz), 134.3, 132.3, 129.9 (t, *J* = 4.4 Hz), 128.6, 113.8 (t, *J* = 26.4 Hz), 112.2 (dt, *J* = 67.6, 25.3 Hz), 110.5 (dt, *J* = 74.1, 25.6 Hz), 108.9 (t, *J* = 24.5 Hz), 48.3 (t, *J* = 5.4 Hz), 45.8, 28.0, 27.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.64 – -111.67 (m, 2F), -114.84 – -114.86 (m, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{14}H_{13}F_4NO_2SNa$, 358.0495; Found, 358.0494.

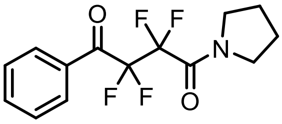


2,2,3,3-tetrafluoro-1-(indolin-1-yl)-4-phenylbutane-1,4-dione (3da): white solid, m.p. = 62°C – 64°C (48.8 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 3H), 7.67 – 7.63 (m, 1H), 7.53 – 7.50 (m, 2H), 7.25 – 7.09 (m, 3H), 4.40 (dd, *J* = 8.0, 8.8 Hz, 2H), 3.24

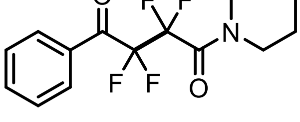
(dd, J = 8.4, 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.0 (t, J = 27.0 Hz), 157.4 (t, J = 25.9 Hz), 141.0, 134.5, 132.2, 131.6, 130.0 (t, J = 3.3 Hz), 128.7, 127.6, 125.7,124.7, 118.0, 114.5 – 113.5 (m), 111.8 – 110.8 (m), 109.1 – 108.1 (m), 47.3 (t, J = 6.9 Hz), 28.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.24 – -114.26 (m, 2F), -115.05 – -115.07 (m, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{18}H_{13}F_4NO_2Na$, 374.0775; Found, 374.0774.



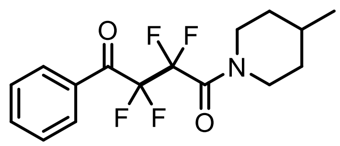
***N, N*-dibutyl-2,2,3,3-tetrafluoro-4-oxo-4-phenylbutanamide (3ea):** pale yellow oil (38.7 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.51 – 7.47 (m, 2H), 3.47 (t, J = 8.4 Hz, 2H), 3.31 (t, J = 7.6 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.57 – 1.49 (m, 2H), 1.41 – 1.24 (m, 4H), 0.97 (t, J = 7.6 Hz, 3H), 0.91 (t, J = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.3 (t, J = 27.0 Hz), 159.6 (t, J = 25.3 Hz), 134.1, 132.6, 129.9, 128.6, 114.0 (t, J = 25.6 Hz), 112.8 – 111.8 (m), 110.6 (dt, J = 88.3, 25.3 Hz), 109.2 (t, J = 24.8 Hz), 47.0 (t, J = 5.2 Hz), 46.6, 30.9, 28.9, 20.0, 19.9, 13.8, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.58 – -111.61 (m, 2F), -114,80 – -114.83 (m, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{18}H_{24}F_4NO_2Na$, 384.1557; Found, 384.1556.



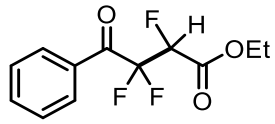
2,2,3,3-tetrafluoro-1-phenyl-4-(pyrrolidin-1-yl) butane-1,4-dione (3fa): pale yellow oil (30.7 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 3.76 (t, J = 6.8 Hz, 2H), 3.50 (t, J = 7.0 Hz, 2H), 1.99 (p, J = 6.8 Hz, 2H), 1.87 (t, J = 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.2 (t, J = 26.7 Hz), 158.4 (t, J = 26.2 Hz), 134.3, 132.4, 130.0 (t, J = 4.4 Hz), 128.6, 113.2 – 112.6 (m), 111.4 – 110.9 (m), 109.6 – 109.1 (m), 47.4, 46.2 (t, J = 5.4 Hz), 26.3, 23.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.86 – -114.89 (m, 2F), -115.42 – -115.45 (m, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{14}H_{13}F_4NO_2Na$, 326.0775; Found, 326.0774.



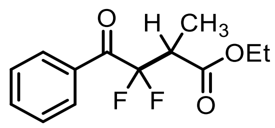
2,2,3,3-tetrafluoro-1-phenyl-4-(piperidin-1-yl) butane-1,4-dione (3ga): pale yellow oil (49.4 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 3.67 (s, 2H), 3.55 – 3.51 (m, 2H), 1.69 (p, J = 3.1 Hz, 4H), 1.63 – 1.58 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.5 (t, J = 27.0 Hz), 158.2 (t, J = 25.3 Hz), 134.0, 132.7, 129.9 (t, J = 4.4 Hz), 128.6, 114.1 (t, J = 26.2 Hz), 112.7 – 112.2 (m), 111.0 – 110.3 (m), 109.0 (t, J = 24.5 Hz), 46.4 (t, J = 5.7 Hz), 44.3, 26.3, 25.4, 24.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.41 – -111.43 (m, 2F), -115.30 – -115.32 (m, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{15}H_{15}F_4NO_2Na$, 340.0931; Found, 340.0930.



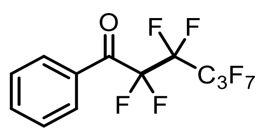
2,2,3,3-tetrafluoro-1-(4-methylpiperidin-1-yl)-4-phenylbutane-1,4-dione (3ha): colorless oil (52.3 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 4.39 – 4.34 (m, 1H), 4.24 – 4.20 (m, 1H), 3.16 – 3.08 (m, 1H), 2.73 – 2.66 (m, 1H), 1.80 – 1.63 (m, 3H), 1.31 – 1.12 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.4 (t, *J* = 26.9 Hz), 158.2 (t, *J* = 25.5 Hz), 134.0, 132.7, 129.8 (t, *J* = 3.3 Hz), 128.5, 115.0 (t, *J* = 26.6 Hz), 113.4 (t, *J* = 24.3 Hz), 112.3 (t, *J* = 26.5 Hz), 110.8 (t, *J* = 24.2 Hz), 109.6 (t, *J* = 26.6 Hz), 108.1 (t, *J* = 24.2 Hz), 45.6 (t, *J* = 5.9 Hz), 43.6, 34.4, 33.4, 30.8, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.34 – -111.37 (m, 2F), -115.25 – -115.28 (m, 2F),; HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{16}H_{17}F_4NO_2Na$, 354.1088; Found, 354.1086.



Ethyl 2,3,3-trifluoro-4-oxo-4-phenylbutanoate (3ia): colorless oil (36.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 8.7, 7.1 Hz, 2H), 5.53 (t, *J* = 10.6 Hz, 1H), 4.33 (qd, *J* = 7.2, 1.8 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9 (t, *J* = 28.1 Hz), 163.8 – 163.4 (m), 134.9, 130.0 (t, *J* = 3.7 Hz), 128.8, 116.8 – 111.1 (m), 86.7 – 83.9 (m), 62.7, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.95 – -110.78 (m), -206.55 (t, *J* = 12.3 Hz); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{12}H_{11}F_3O_3Na$, 283.0553; Found, 283.0551.

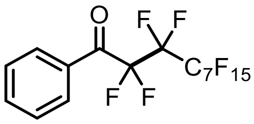


Ethyl 3,3-difluoro-2-methyl-4-oxo-4-phenylbutanoate (3ja)[4]: colorless oil (33.3 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 8.4, 7.1 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.62 – 3.49 (m, 1H), 1.46 (d, *J* = 7.3 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6 – 188.8 (m), 170.1 (d, *J* = 11.0 Hz), 134.1, 132.3, 130.3 – 129.7 (m), 128.6, 117.8 (dd, *J* = 262.8, 253.6 Hz), 61.3, 44.2 – 43.5 (m), 13.9, 9.8 (t, *J* = 4.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.80 – -110.09 (m, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{14}F_2O_3Na$, 279.0803; Found, 279.0801.

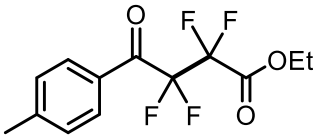


2,2,3,3,4,4,5,5,6,6,6-undecafluoro-1-phenylhexan-1-one (3ka)[5]: colorless oil (51.7 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3 (t, *J* = 25.9 Hz), 135.4, 131.6, 130.2 (t, *J* = 4.0 Hz), 129.0, 121.5 – 105.6 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.89 (t, *J* = 12.3 Hz, 3F), -112.83 (t, *J* = 14.3 Hz, 2F), -121.12 – -121.26 (m, 2F), -121.86 – -122.06 (m, 2F), -126.26

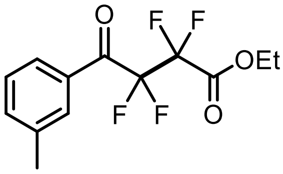
– -126.37 (m, 2F); HRMS (ESI) *m/z*: $[M + K]^+$ Calcd. for $C_{12}H_5F_{11}OK$, 412.9796; Found, 412.9796.



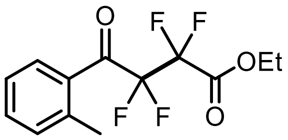
2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro-1-phenyldecan-1-one (3la): colorless oil (85.1 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3 (t, *J* = 26.0 Hz), 135.3, 131.7, 130.2 (t, *J* = 3.9 Hz), 129.0, 121.5 (t, *J* = 33.2 Hz), 118.6 (t, *J* = 33.0 Hz), 115.7 (t, *J* = 33.0 Hz), 114.2 – 112.5 (m), 111.7 – 110.3 (m), 109.0 – 107.2 (m), 106.3 – 105.2 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.24 – -81.33 (m, 3F), -112.91 – -113.00 (m, 2F), -121.06 – -123.07 (m, 12F), -123.01 – -123.07 (m, 2F); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{16}H_6F_{19}O$, 575.0110; Found, 575.0111.



Ethyl 2,2,3,3-tetrafluoro-4-oxo-4-(p-tolyl) butanoate (3ab): colorless oil (40.9 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.0 (t, *J* = 27.3 Hz), 159.8 (t, *J* = 29.5 Hz), 147.0, 130.3 (t, *J* = 3.5 Hz), 129.7, 129.5, 128.5, 113.9 (t, *J* = 28.6 Hz), 111.5 – 110.5 (m), 108.8 – 107.9 (m), 105.5 (t, *J* = 28.1 Hz), 63.8, 21.9, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.99 (t, *J* = 4.8 Hz, 2F), -120.62 (t, *J* = 4.8 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{12}F_4O_3Na$, 315.0615; Found, 315.0614.

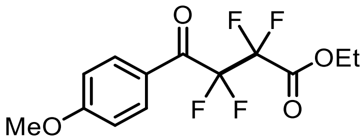


Ethyl 2,2,3,3-tetrafluoro-4-oxo-4-(m-tolyl) butanoate (3ac): colorless oil (43.8 mg, 75% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.6 (t, *J* = 27.7 Hz), 159.8 (t, *J* = 29.5 Hz), 139.0, 136.3, 131.0, 130.5, 128.8, 127.5 (t, *J* = 3.9 Hz), 113.8, 111.4 – 110.7 (m), 108.4 – 107.8 (m), 105.5, 63.8, 21.3, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.98 (t, *J* = 6.5 Hz, 2F), -120.53 (t, *J* = 6.5 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{12}F_4O_3Na$, 315.0615; Found, 315.0614.

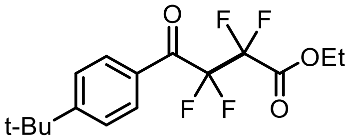


Ethyl 2,2,3,3-tetrafluoro-4-oxo-4-(o-tolyl) butanoate (3ad): colorless oil (45.4 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.0 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101

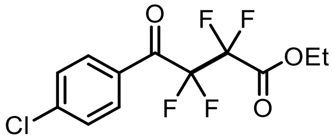
MHz, $CDCl_3$) δ 188.2 (t, *J* = 26.6 Hz), 159.9 (t, *J* = 29.7 Hz), 141.4, 133.7, 132.4, 130.7, 130.1 (t, *J* = 5.9 Hz), 125.8, 113.3 (t, *J* = 28.1 Hz), 111.3 – 110.4 (m), 108.6 – 107.7 (m), 105.7 (t, *J* = 28.3 Hz), 63.8, 21.3, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9 (t, *J* = 5.1 Hz, 2F), -120.2 (t, *J* = 5.1 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{13}F_4O_3Na$, 315.0615; Found, 315.0614.



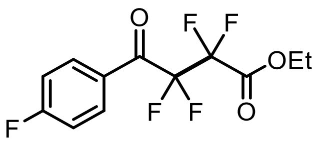
Ethyl 2,2,3,3-tetrafluoro-4-(4-methoxyphenyl)-4-oxobutanoate (3ae): colorless oil (27.5 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.7 Hz, 2H), 7.01 – 6.98 (m, 2H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7 (t, *J* = 27.0 Hz), 165.4, 159.9 (t, *J* = 29.7 Hz), 132.8 (t, *J* = 3.9 Hz), 123.8, 114.3 – 113.8 (m), 111.6 – 110.5 (m), 108.7 – 107.9 (m), 105.5 (t, *J* = 27.2 Hz), 63.7, 55.7, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.59 (t, *J* = 6.5 Hz, 2F), -120.78 (t, *J* = 6.8 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{12}F_4O_4Na$, 331.0564; Found, 331.0563.



Ethyl 4-(4-(tert-butyl) phenyl)-2,2,3,3-tetrafluoro-4-oxobutanoate (3af): colorless oil (53.5 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.38 – 1.34 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.0 (t, *J* = 27.1 Hz), 160.1 – 159.5 (m), 130.2 (t, *J* = 3.5 Hz), 128.4 (d, *J* = 3.3 Hz), 126.0, 113.9 (t, *J* = 28.4 Hz), 111.5 – 110.8 (m), 108.5 – 107.9 (m), 105.5 (t, *J* = 28.1 Hz), 63.8, 35.4, 30.9, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.99 (t, *J* = 5.8 Hz, 2F), -120.60 (t, *J* = 6.1 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{16}H_{18}F_4O_3Na$, 357.1084; Found, 357.1083.

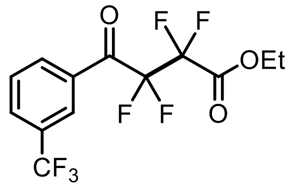


Ethyl 4-(4-chlorophenyl)-2,2,3,3-tetrafluoro-4-oxobutanoate (3ag): colorless oil (43.1 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.50 (m, 2H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3 (t, *J* = 27.7 Hz), 159.6 (t, *J* = 29.5 Hz), 142.4, 131.5 (t, *J* = 3.7 Hz), 129.4, 129.4 – 129.3 (m), 131.5 (t, *J* = 3.7 Hz), 111.3 – 110.4 (m), 108.6 – 107.8 (m), 105.4 (t, *J* = 28.1 Hz), 63.9, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.37 (t, *J* = 6.1 Hz, 2F), -120.31 (t, *J* = 6.1 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{12}H_9ClF_4O_3Na$, 335.0069; Found, 335.0068.

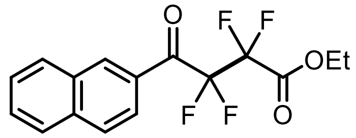


Ethyl 2,2,3,3-tetrafluoro-4-(4-fluorophenyl)-4-oxobutanoate (3ah): pale yellow oil (47.4 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.14 (m, 2H), 7.25 – 7.19 (m, 2H), 4.42

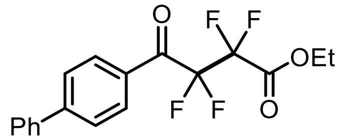
(q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9 (t, J = 27.5 Hz), 168.4, 165.8, 159.7 (t, J = 29.3 Hz), 133.2 (dt, J = 9.9, 3.3 Hz), 127.4 (d, J = 3.7 Hz), 116.5, 116.3, 113.7 (t, 28.0 Hz), 111.3 – 110.4 (m), 108.7 – 107.8 (m), 105.4 (t, J = 27.8 Hz), 63.9, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.81 (s, 1F), -113.16 (t, J = 6.8 Hz, 2F), -120.44 (t, J = 6.5 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{12}H_9F_5O_3Na$, 319.0364; Found, 319.0362.



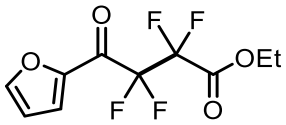
Ethyl 2,2,3,3-tetrafluoro-4-oxo-4-(3-(trifluoromethyl) phenyl) butanoate (3ai): colorless oil (44.1 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.29 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.72 (t, J = 7.9 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4 (t, J = 27.9 Hz), 159.6 (t, J = 29.3 Hz), 133.2 (d, J = 4.4 Hz), 132.4 – 131.4 (m), 129.8, 127.3 – 119.2 (m), 113.6 (t, J = 28.9 Hz), 111.2 – 110.4 (m), 108.5 – 107.7 (m), 105.4 (t, J = 28.3 Hz),64.1, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.28(s, 3F), -113.77 (t, J = 5.6 Hz, 2F), -120.16 (t, J = 5.3 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_9F_7O_3Na$, 369.0332; Found, 369.0332.



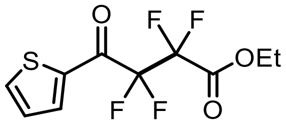
Ethyl 2,2,3,3-tetrafluoro-4-(naphthalen-2-yl)-4-oxobutanoate (3aj): colorless oil (39.0 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.07 – 8.01 (m, 2H), 7.96 – 7.90 (m, 2H), 7.71 – 7.67 (m, 1H), 7.63 – 7.59 (m, 1H), 4.43 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9 (t, J = 27.3 Hz), 159.8 (t, J = 29.5 Hz), 148.1, 139.1, 130.8 (t, J = 3.5 Hz), 129.6, 129.1, 128.8, 127.5, 127.3, 113.9, 111.0 (dt, J = 40.0, 28.5 Hz), 108.5 – 107.9 (m), 105.5, 63.8, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.38 (t, J = 6.5 Hz, 2F), -120.39 (t, J = 6.5 Hz, 2F); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{16}H_{13}F_4O_3$, 329.0795; Found, 329.0794.



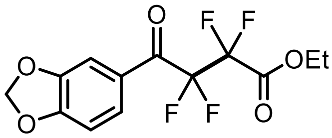
Ethyl 4-([1,1'-biphenyl]-4-yl)-2,2,3,3-tetrafluoro-4-oxobutanoate (3ak): colorless oil (48.6 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.50 – 7.41 (m, 3H), 4.42 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9 (t, J = 27.3 Hz), 159.8 (t, J = 29.5 Hz), 148.1, 139.1, 130.8 (t, J = 3.5 Hz), 129.6 (d, J = 3.3 Hz), 129.1, 128.8, 127.5, 127.3, 113.9, 111.5 – 110.5 (m), 108.7 – 107.2 (m), 105.5, 63.8, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.99 (t, J = 5.2 Hz, 2F), -120.39 (t, J = 5.3 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{18}H_{14}F_4O_3Na$, 377.0771; Found, 377.0771



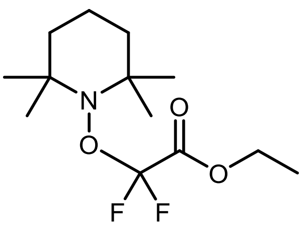
Ethyl 2,2,3,3-tetrafluoro-4-(furan-2-yl)-4-oxobutanoate (3al): colorless oil (9.3 mg, 17% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.59 – 7.54 (m, 1H), 6.68 (dd, *J* = 3.8, 1.7 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5 (t, *J* = 27.8 Hz), 159.4 (t, *J* = 29.4 Hz), 150.1, 147.8, 124.7, 113.2, 112.1 (t, *J* = 30.0 Hz), 110.1 (dt, *J* = 69.8, 29.4 Hz), 108.4 (dt, *J* = 66.3, 30.5 Hz), 106.4 (t, *J* = 30.0 Hz), 64.1, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.99 (t, *J* = 5.8 Hz, 2F), -120.05 (t, *J* = 5.8 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{10}H_8F_4O_4Na$, 291.0251; Found, 291.0249.



Ethyl 2,2,3,3-tetrafluoro-4-oxo-4-(thiophen-2-yl) butanoate (3am): pale yellow oil (17.5 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 1H), 7.90 (d, *J* = 4.9 Hz, 1H), 7.27 – 7.24 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.97 (t, *J* = 27.9 Hz), 159.50 (t, *J* = 29.5 Hz), 138.03, 137.48, 136.81 (t, *J* = 5.1 Hz), 129.18, 113.30, 110.70 (td, *J* = 29.8, 14.9 Hz), 108.05 (td, *J* = 30.0, 29.5, 19.6 Hz), 105.52 (t, *J* = 29.5 Hz), 64.03, 13.73; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.78 (t, *J* = 5.8 Hz, 2F), -120.11 (t, *J* = 6.1 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{10}H_8F_4O_3SNa$, 307.0022; Found, 307.0020.



Ethyl 4-(benzo[*d*] [1,3] dioxol-5-yl)-2,2,3,3-tetrafluoro-4-oxobutanoate (3an): colorless oil (33.4 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.50 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.10 (s, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3 (t, *J* = 27.3 Hz), 159.8 (t, *J* = 29.7 Hz), 154.0, 148.5, 127.9 (t, *J* = 4.4 Hz), 125.3, 113.9 (t, *J* = 28.1 Hz), 111.5 – 110.4 (m), 109.3, 108.5 – 107.8 (m), 105.5 (t, *J* = 27.8 Hz), 102.4, 63.7, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.26 (t, *J* = 6.5 Hz, 2F), -120.69 (t, *J* = 6.8 Hz, 2F); HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd. for $C_{13}H_{10}F_4O_5Na$, 345.0357; Found, 345.0355.



Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl) oxy) acetate (4)[6]: colorless oil (35.6 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (q, *J* = 7.1 Hz, 2H), 1.60 – 1.55 (m, 5H), 1.37 (t, *J* = 7.2 Hz, 4H), 1.20 – 1.17 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (t, *J*

= 42.6 Hz), 114.5 (t, *J* = 271.5 Hz), 62.0, 60.4, 39.2, 32.4, 29.9, 19.7, 15.9, 12.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.5(s, 2F); HRMS (ESI) *m/z*: $[M + H]^+$ Calcd. for $C_{13}H_{24}F_2NO_3$, 280.1719; Found, 280.1718.

11. Reference

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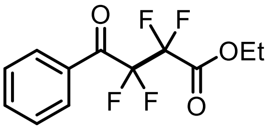
12. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of all new products[a]

[a] ^{1}H NMR was conducted in 400MHz, ^{19}F NMR was conducted in 376 MHz and ^{13}C NMR was conducted in 101MHz unless noted.



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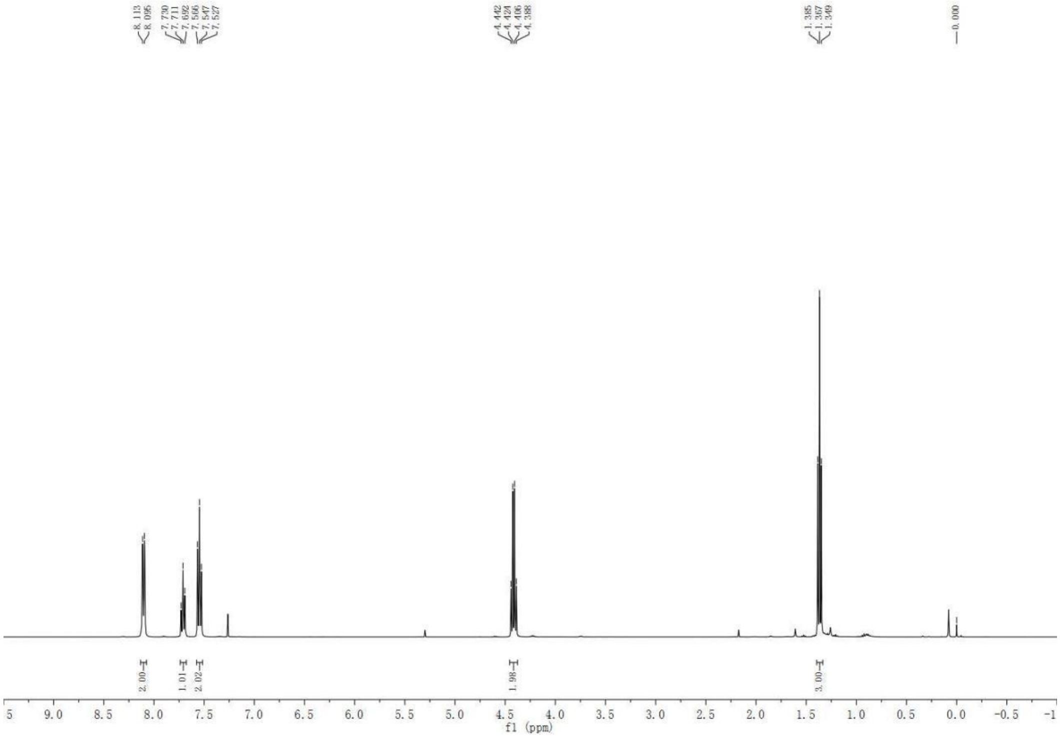

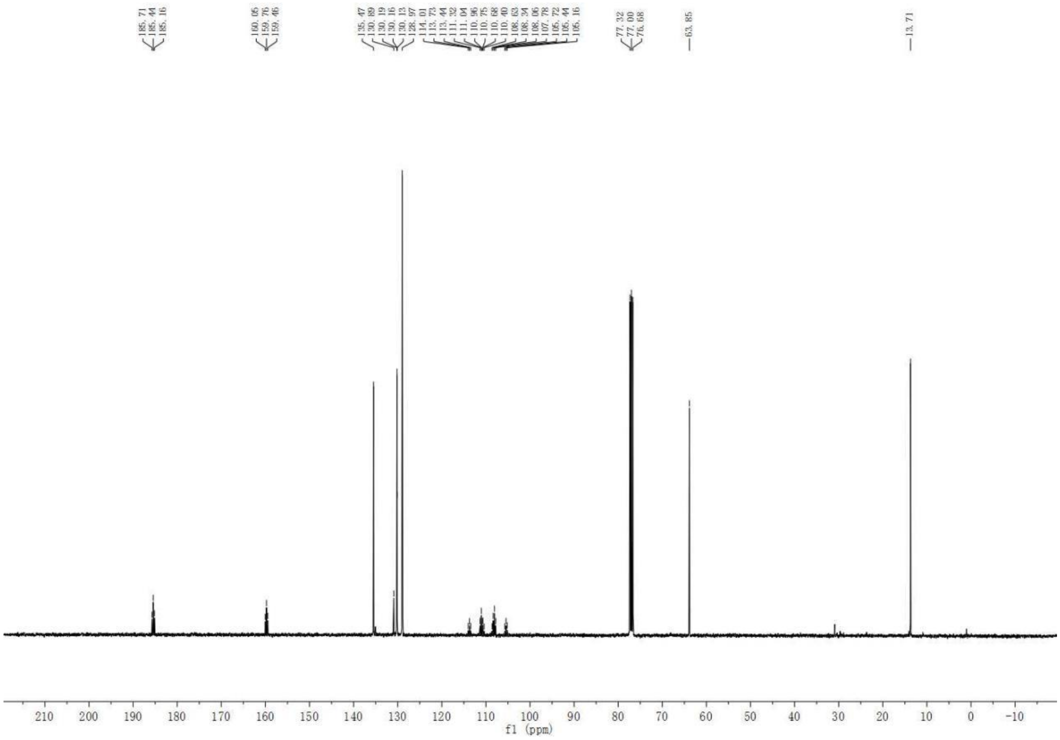

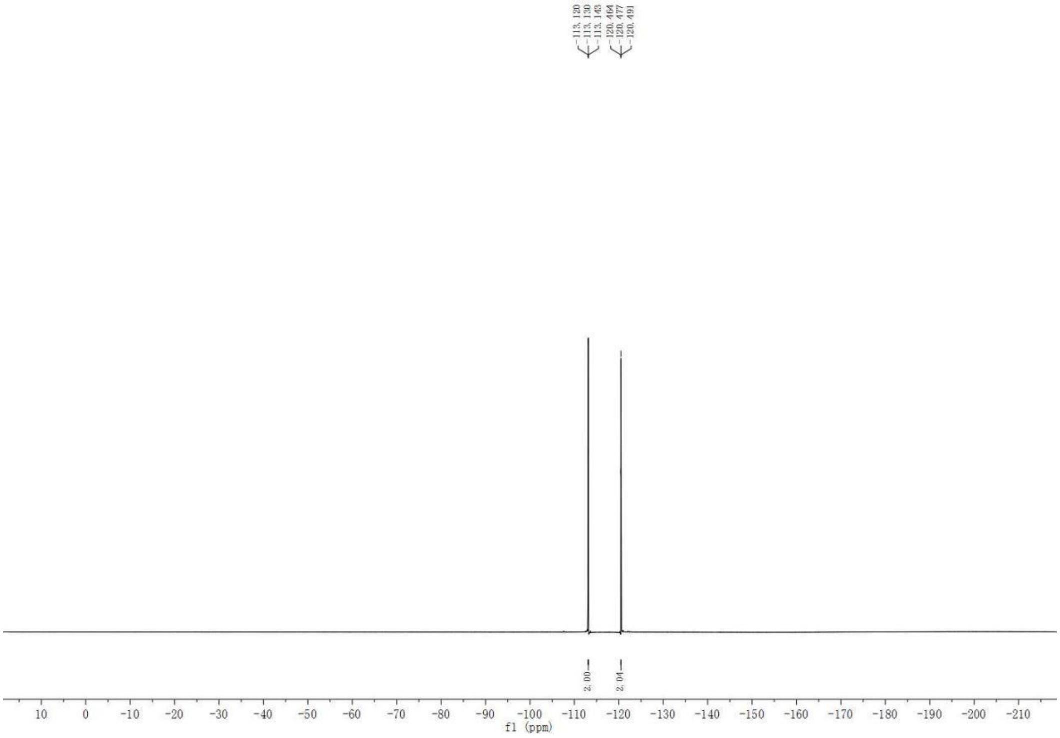
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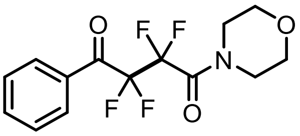

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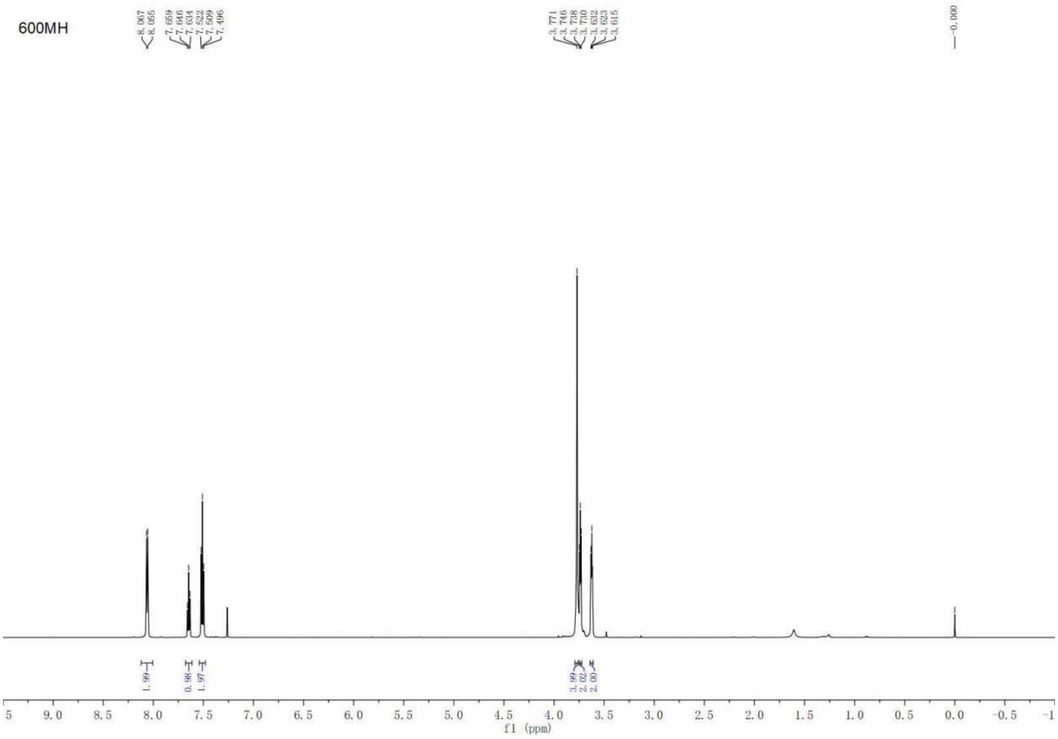

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3.632
3.623
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0.000
1.99
0.98
1.97
3.99
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2.00
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7.0
6.5
6.0
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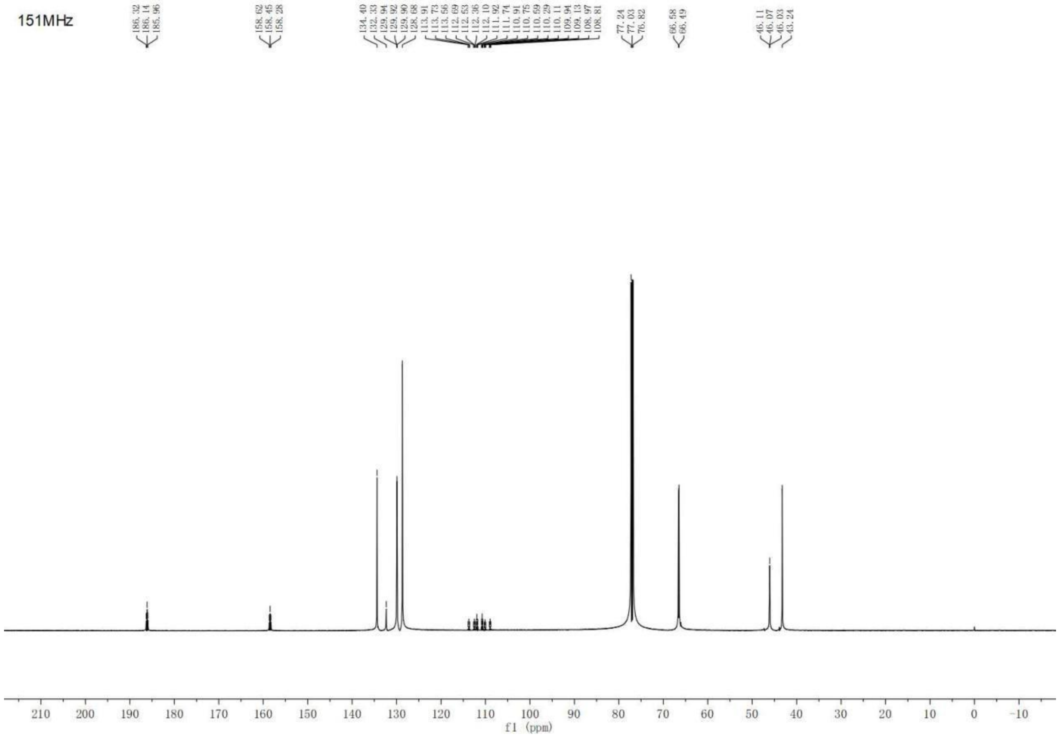
f1 (ppm)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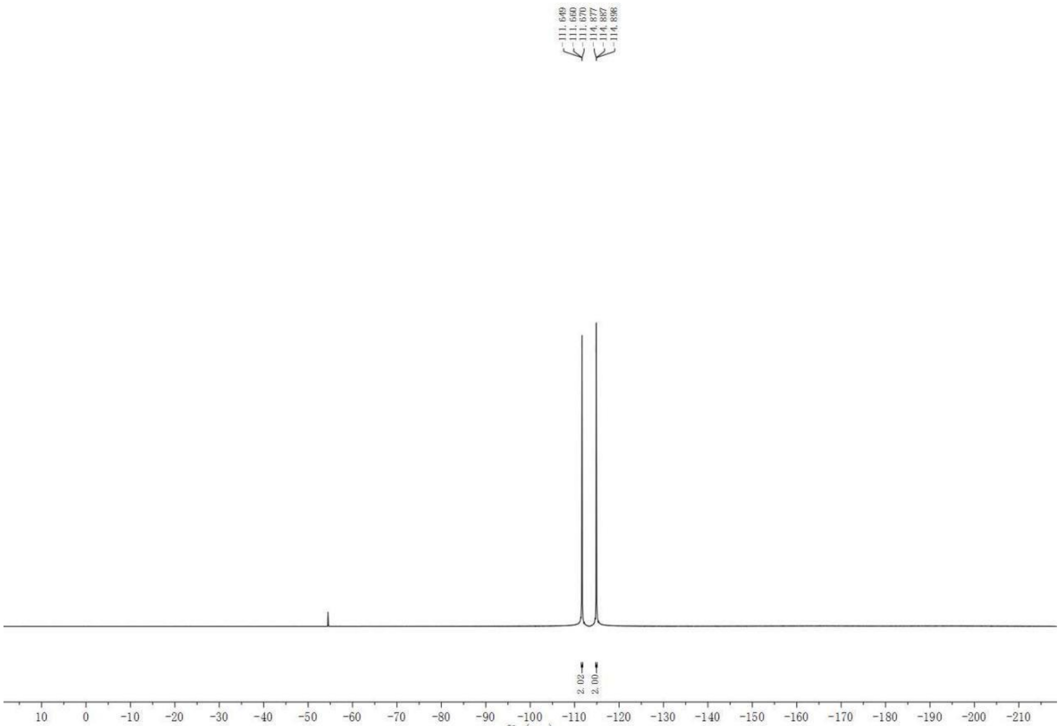

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-60
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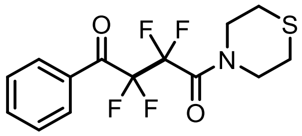
-200
-210
f1 (ppm)



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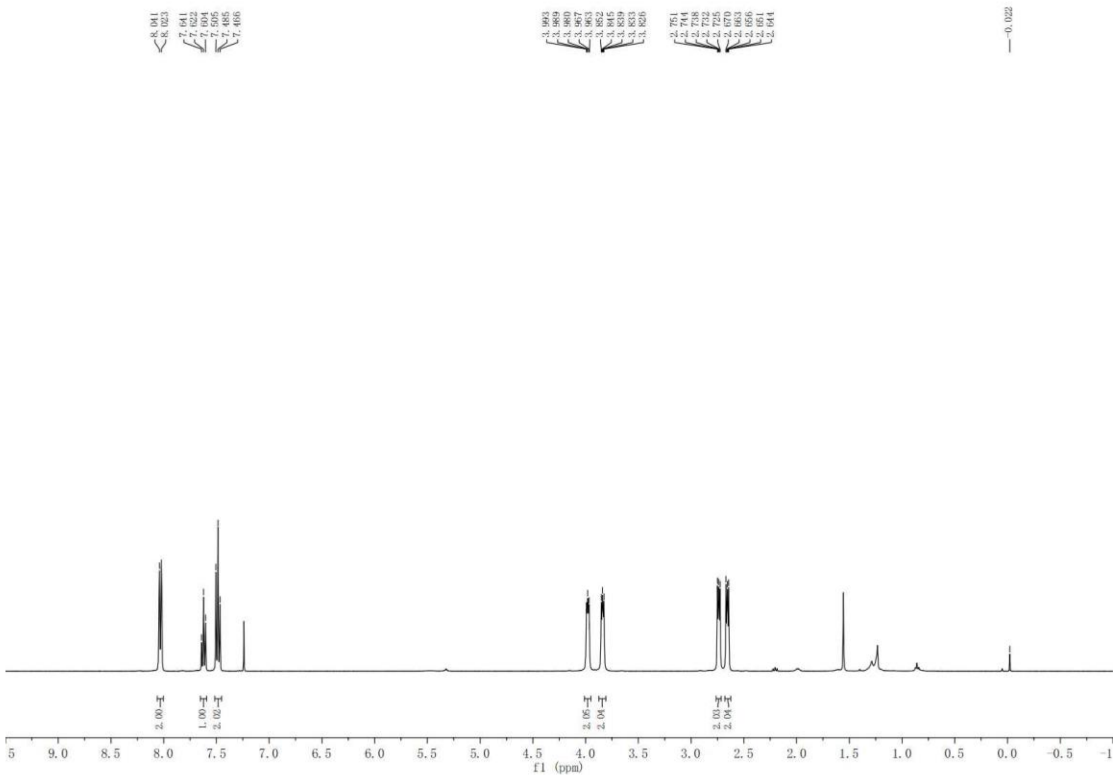

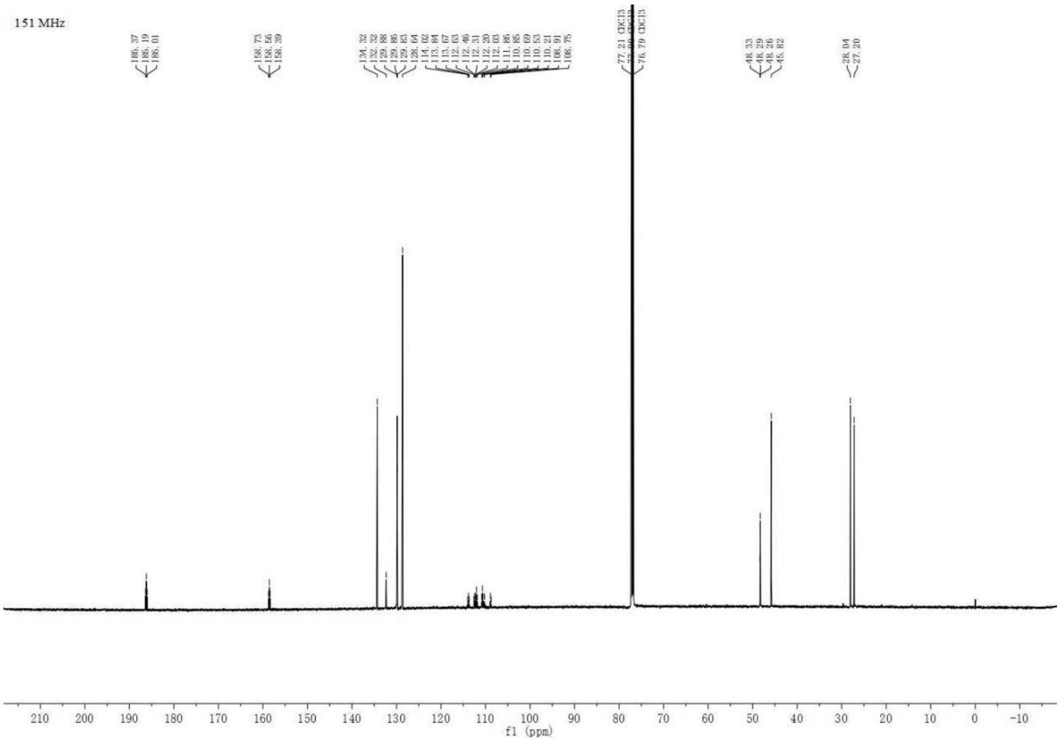

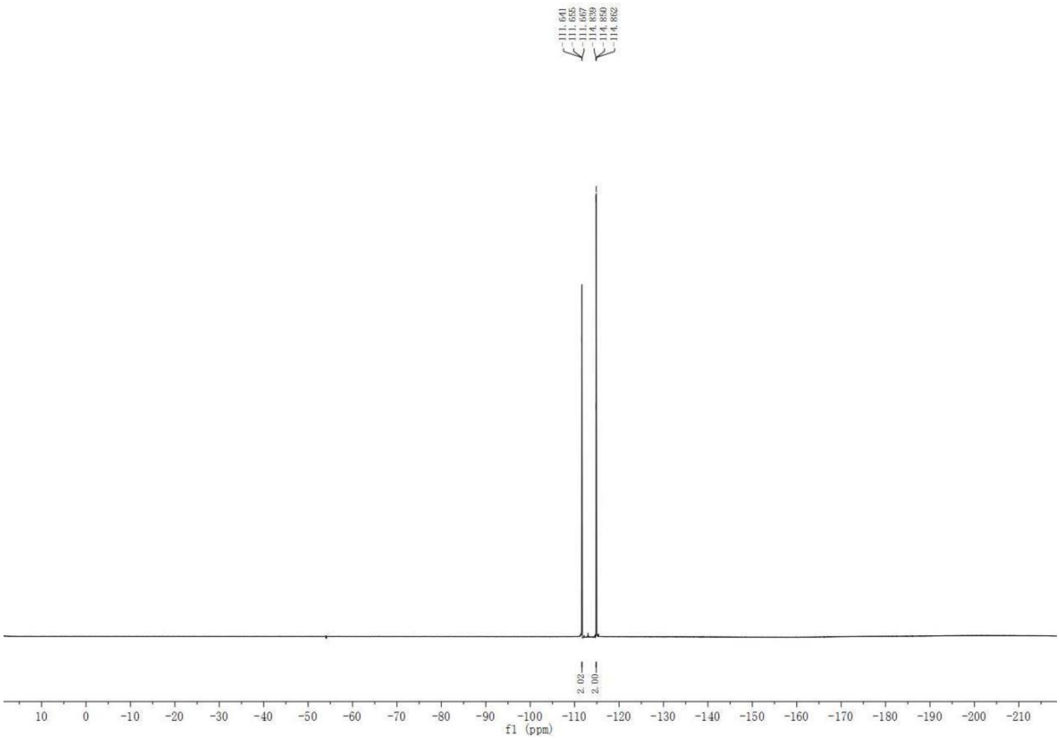
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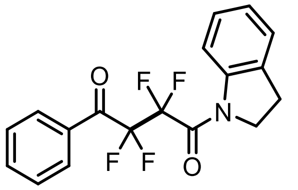
f1 (ppm)



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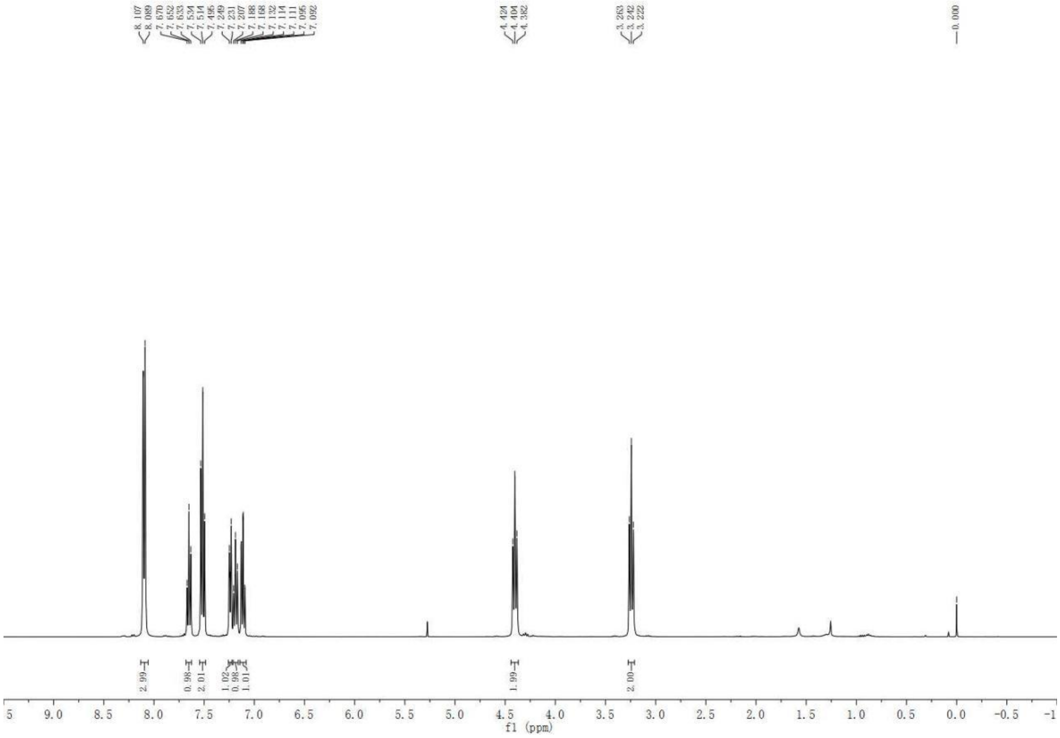

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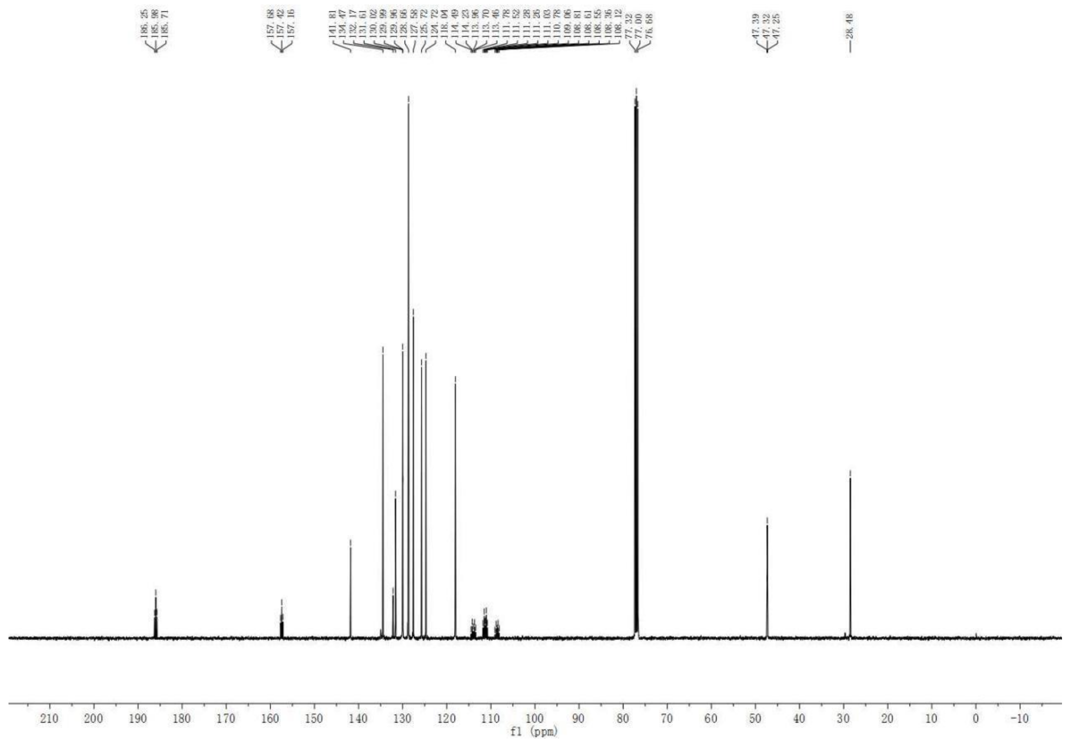

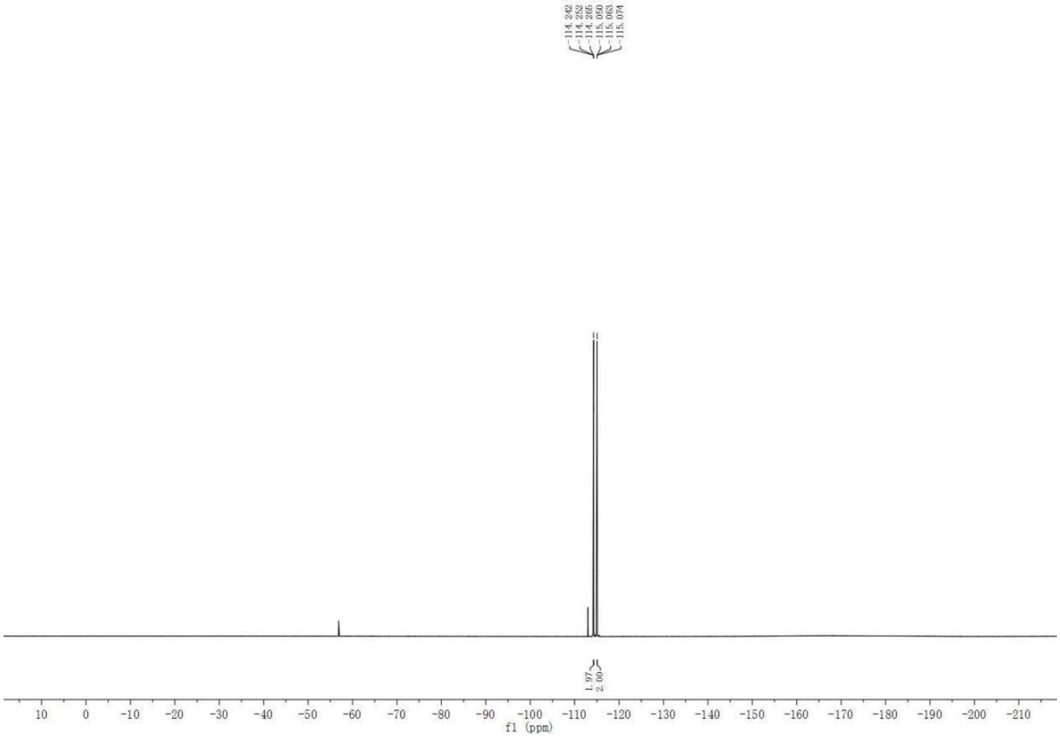
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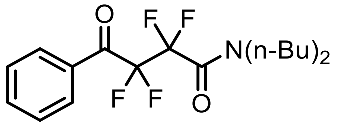

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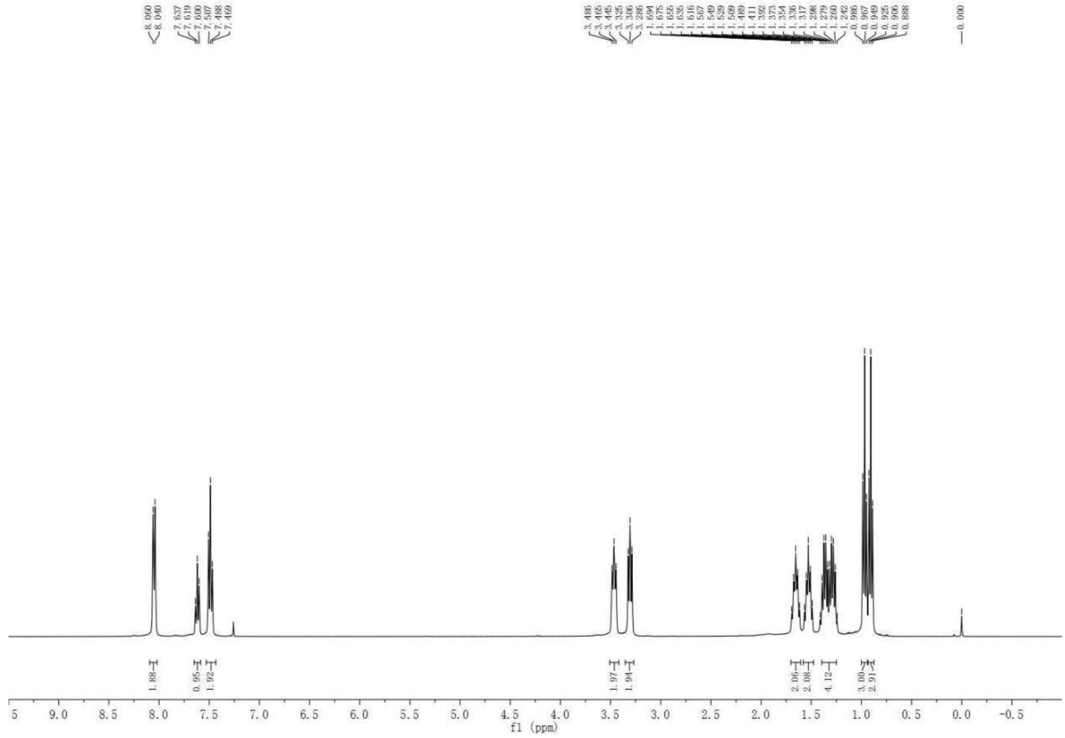

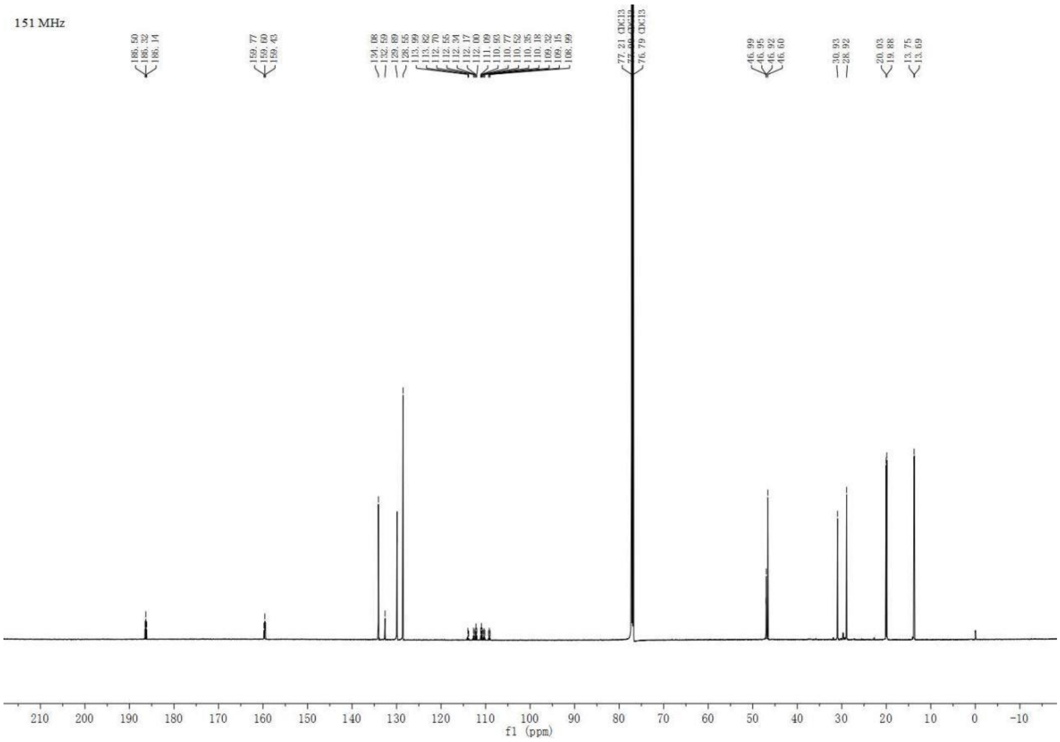

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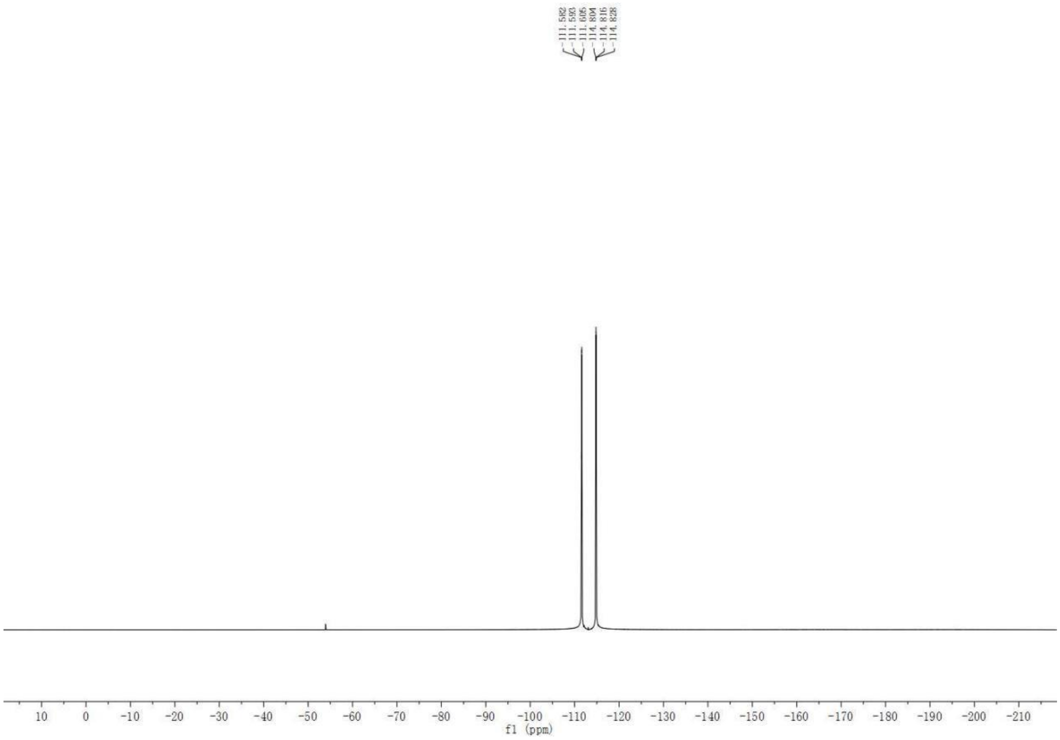
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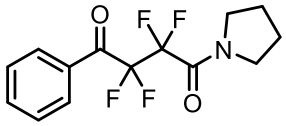

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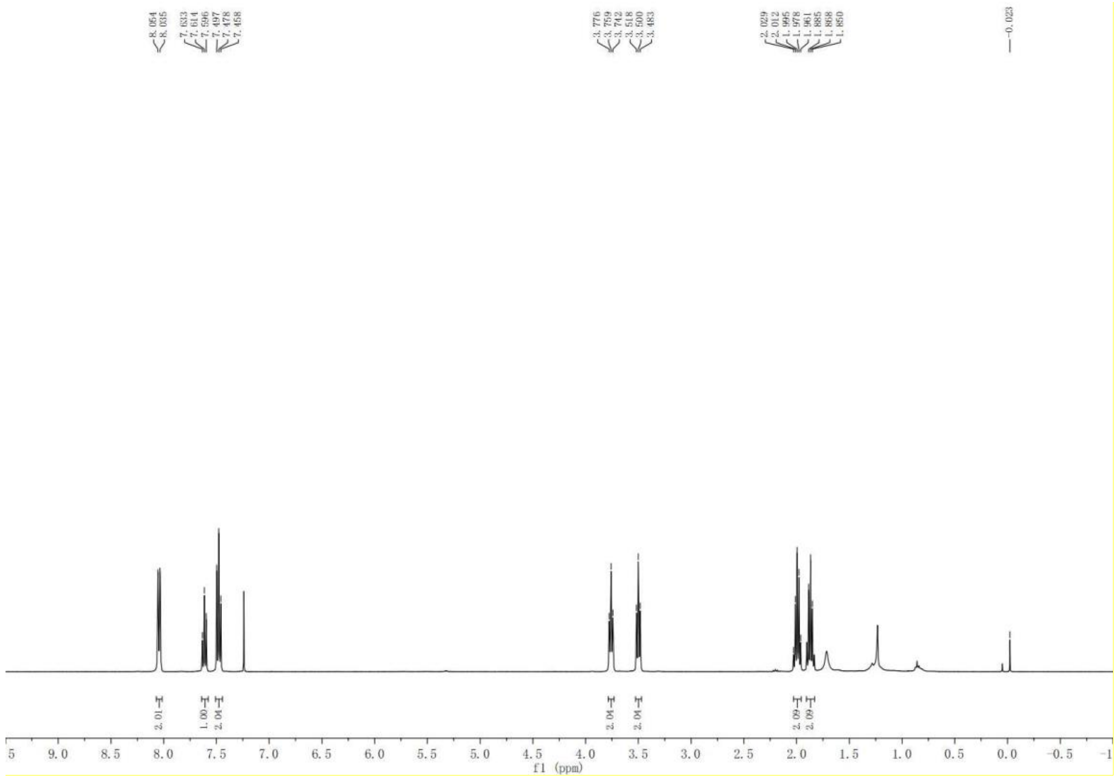

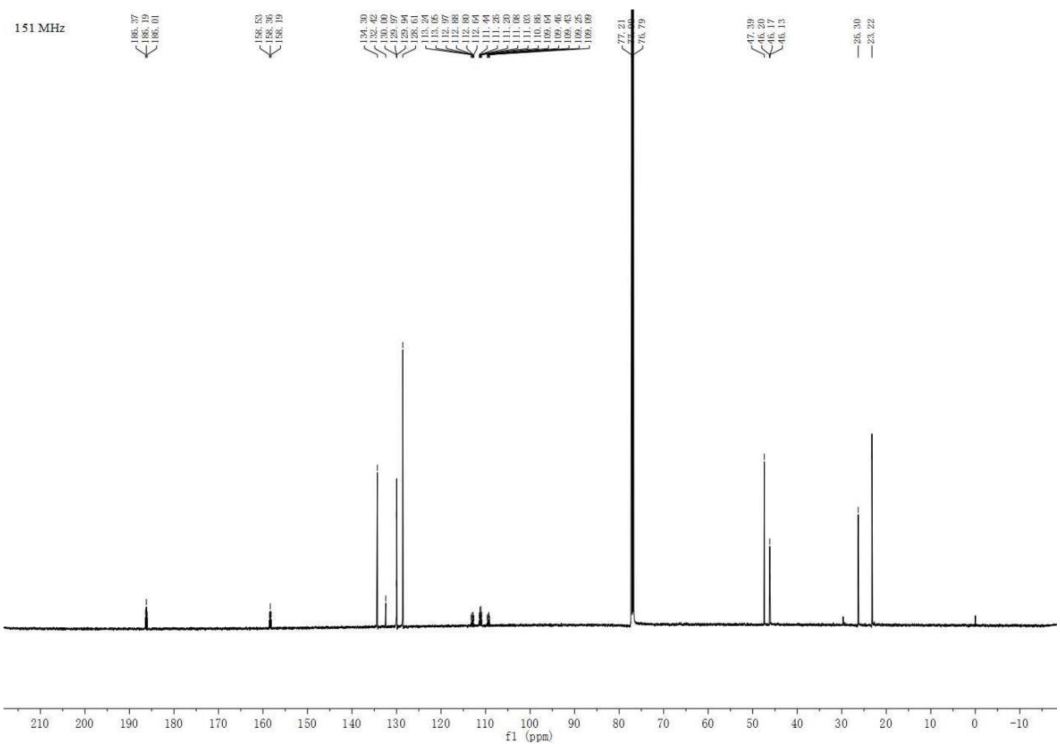
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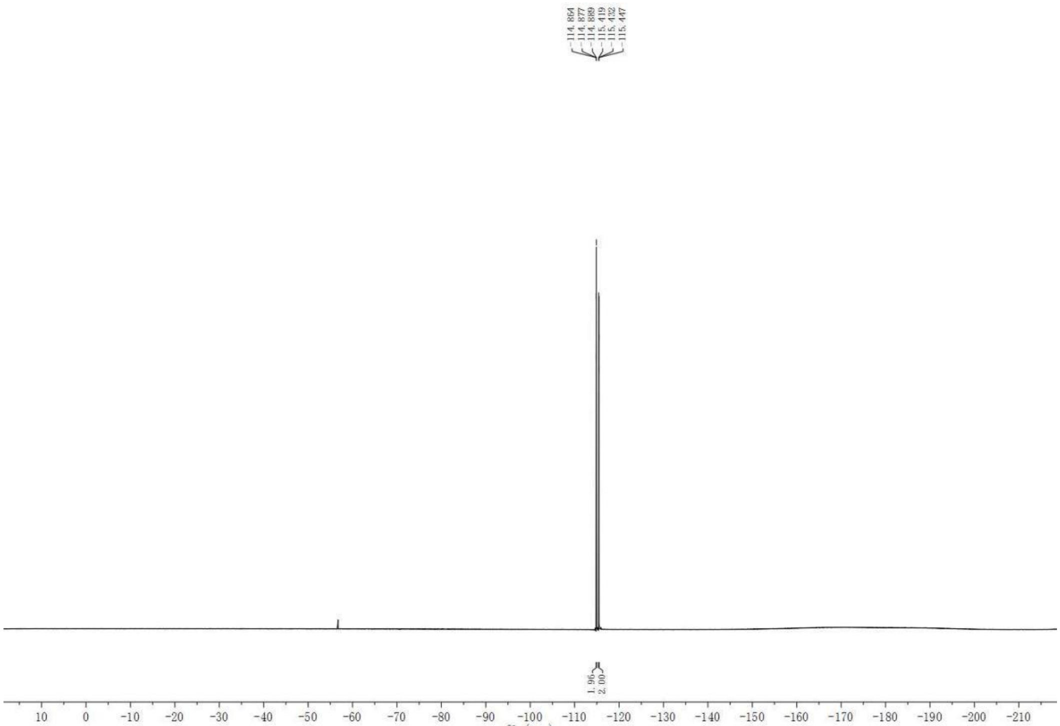
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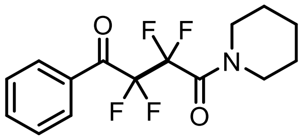

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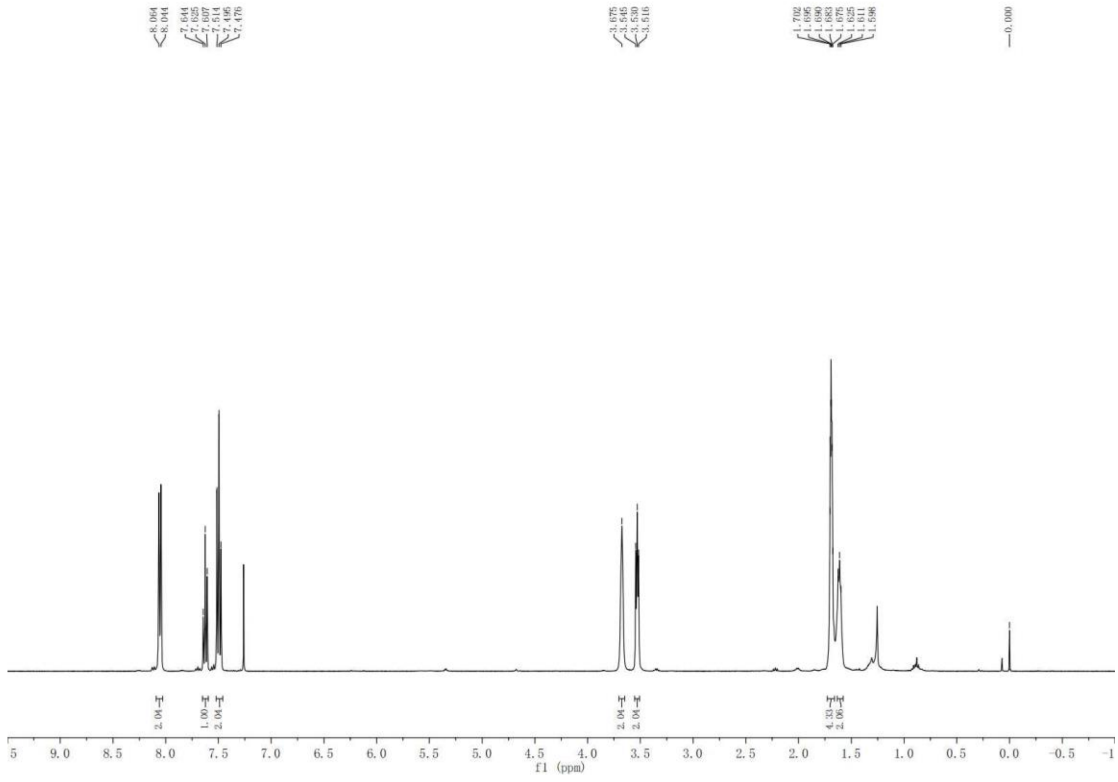

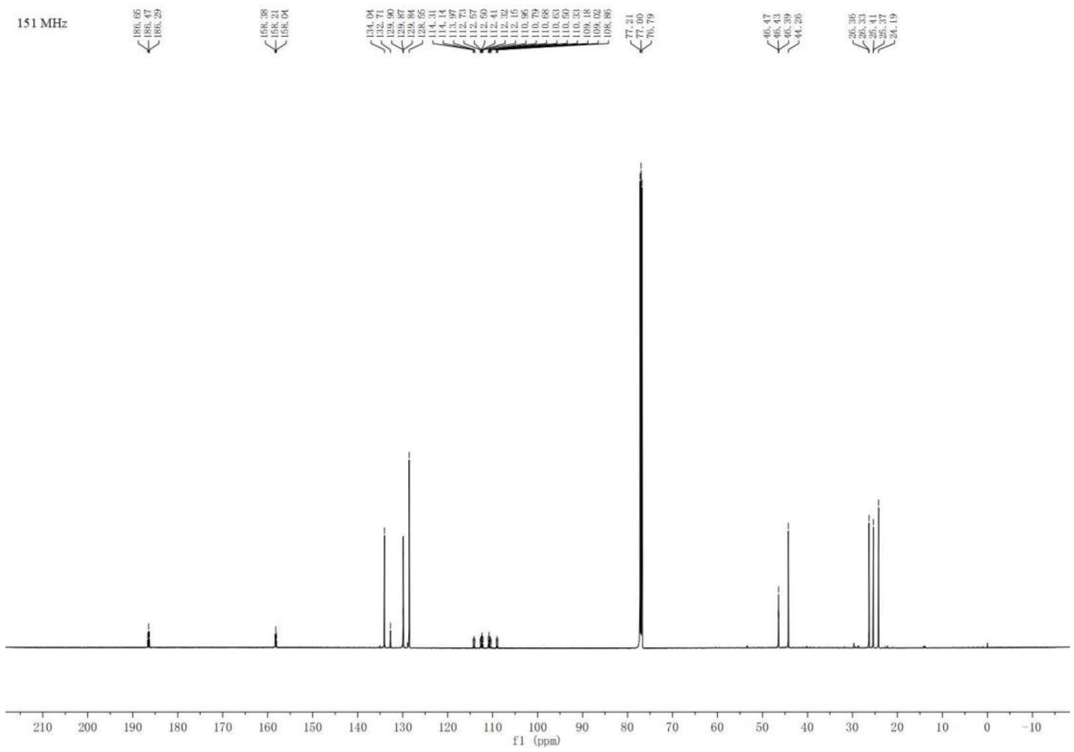
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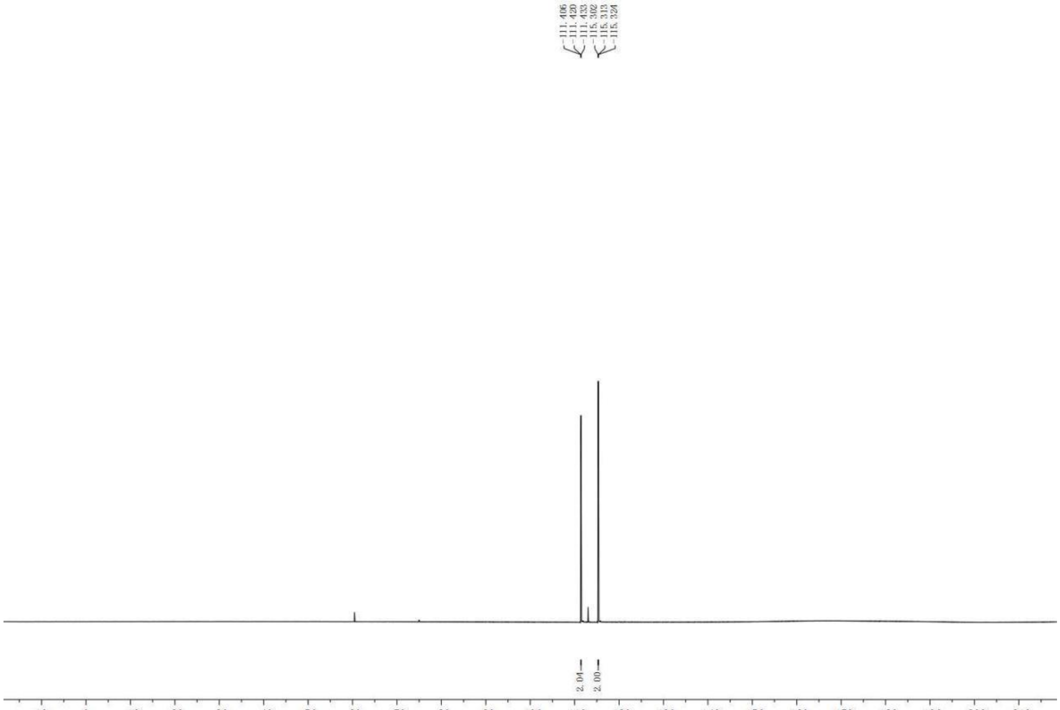
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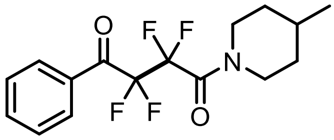

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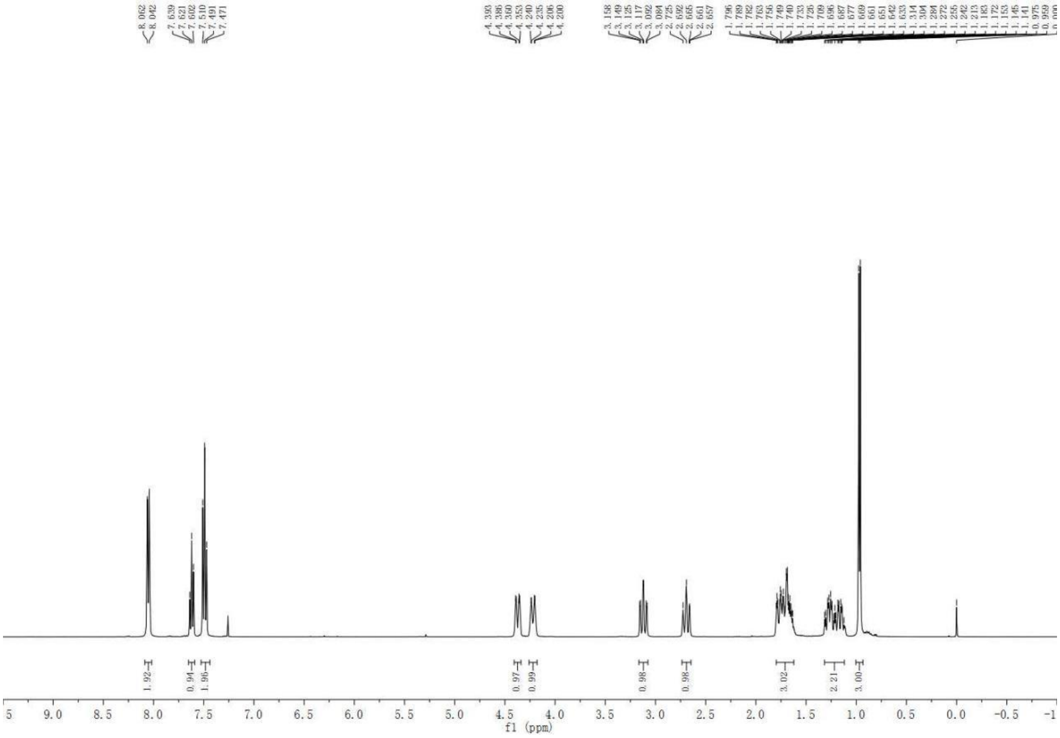

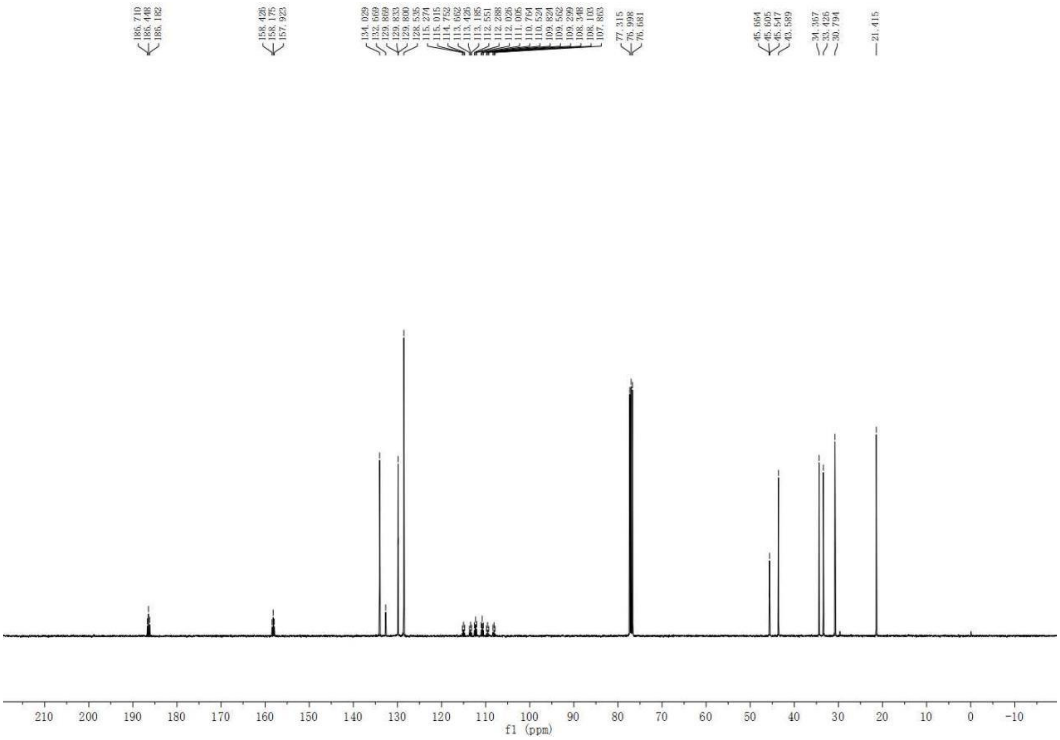
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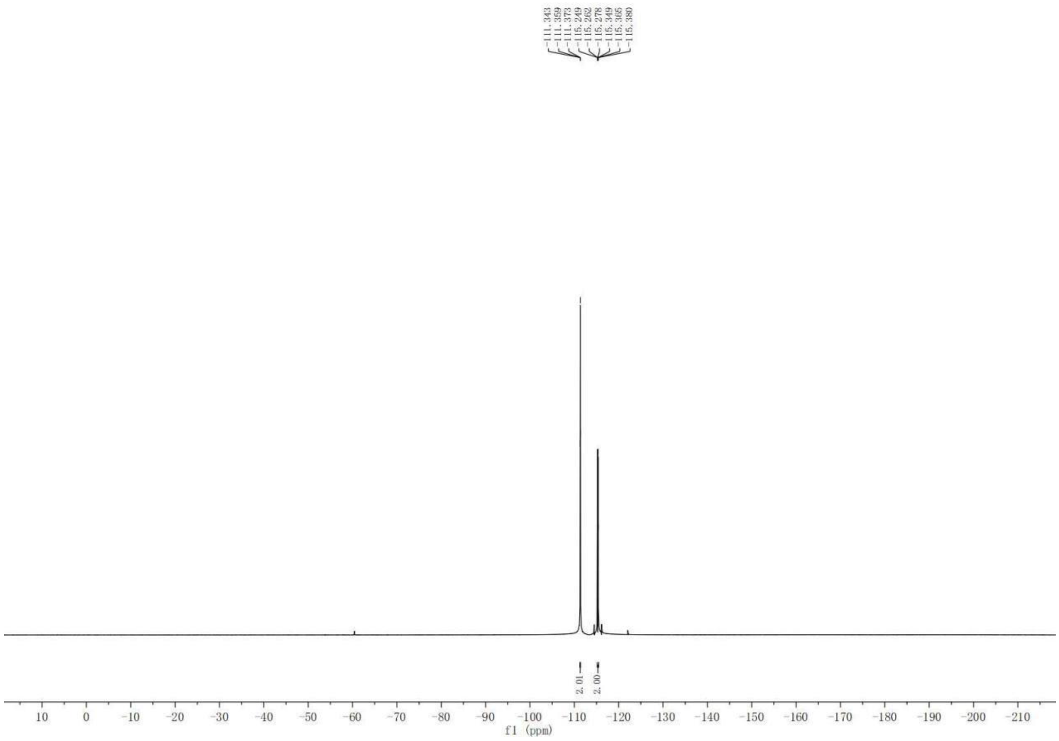
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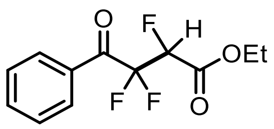
2.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



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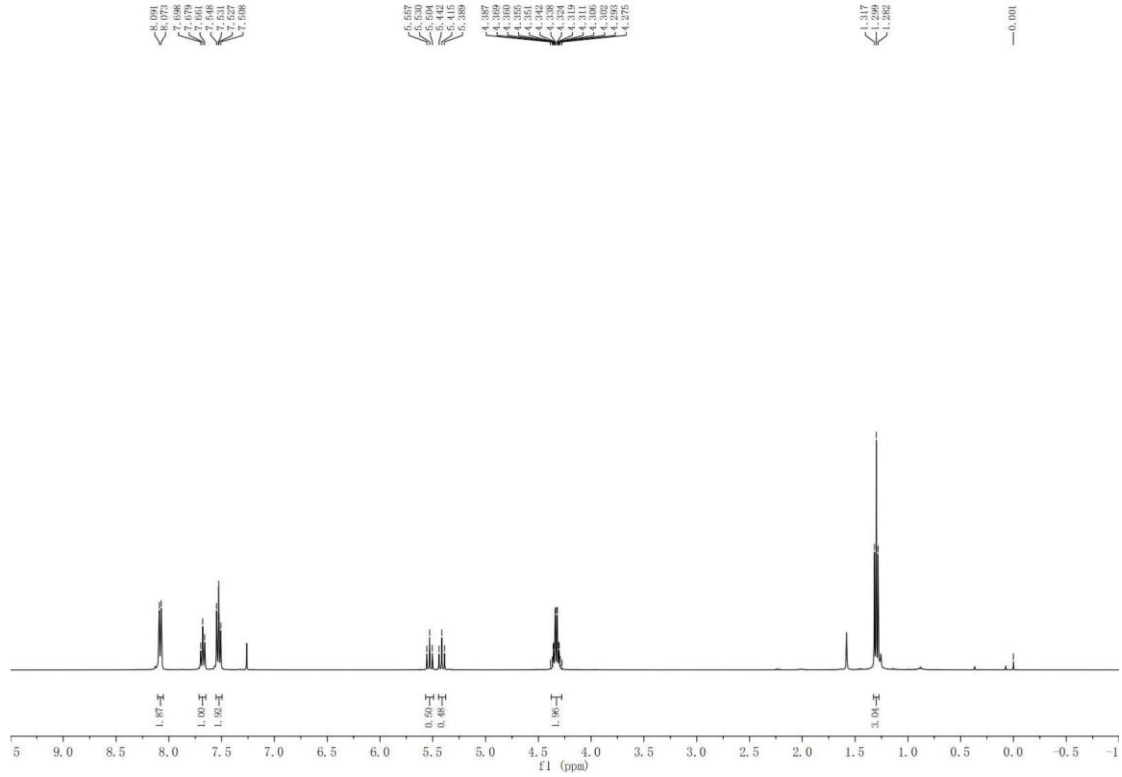
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8.073
7.698
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7.548
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7.527
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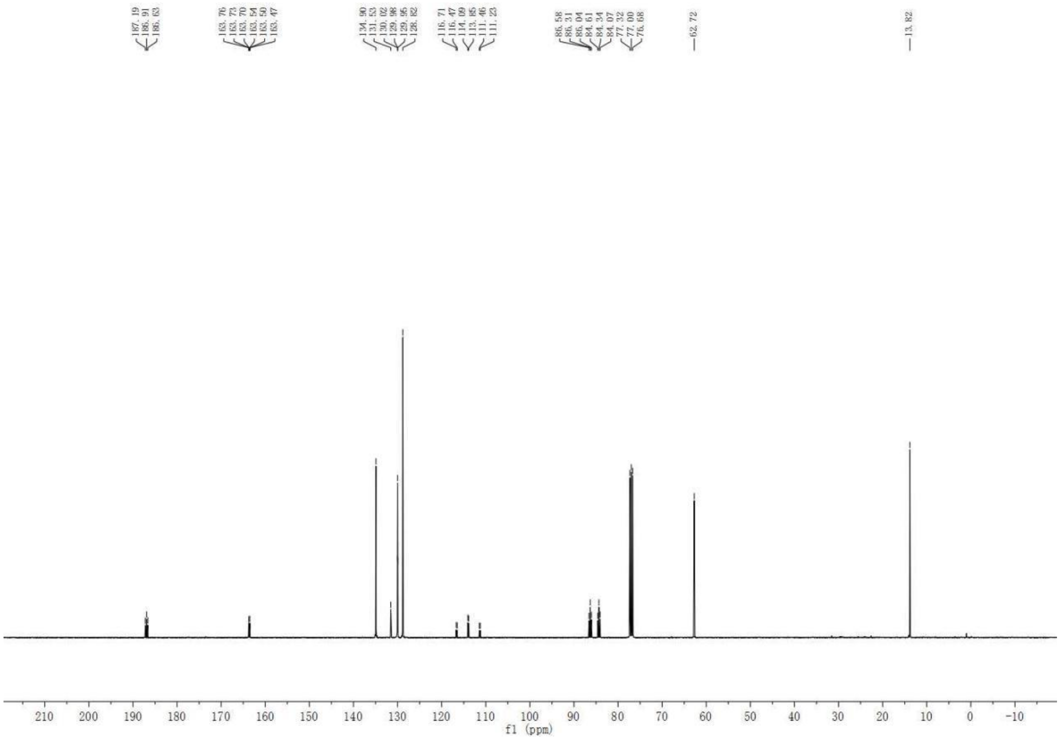
5.557
5.530
5.504
5.442
5.415
5.389
4.387
4.369
4.360
4.355
4.351
4.342
4.338
4.324
4.319
4.311
4.306
4.302
4.293
4.275
1.317
1.299
1.282
0.001
1.87
1.00
1.92
0.50
0.48
1.96
3.04
f1 (ppm)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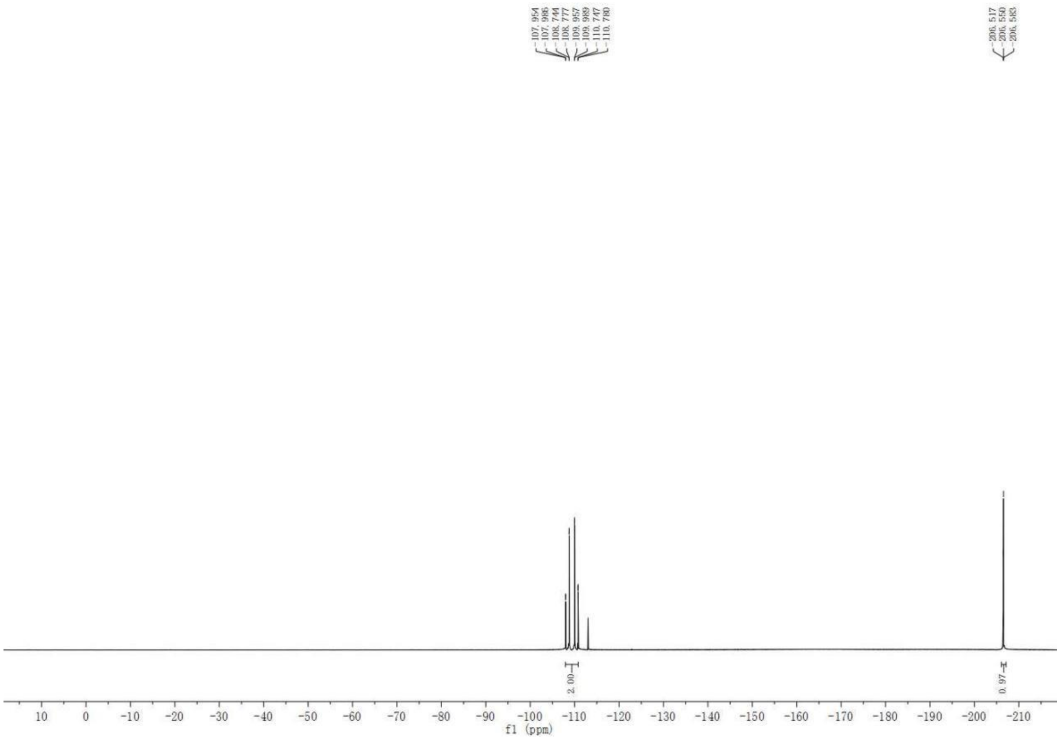
163.54
163.50
163.47
134.90
131.53
130.02
129.98
129.95
128.82
116.71
116.47
114.09
113.85
111.46
111.23
86.58
86.31
85.04
84.61
84.34
84.07
77.32
77.00
76.68
62.72
13.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-107.986
-108.744
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-109.957
-109.989
-110.747
-110.780
-206.517
-206.550
-206.583
2.00
0.97
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
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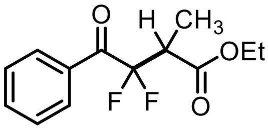
-200
-210
f1 (ppm)



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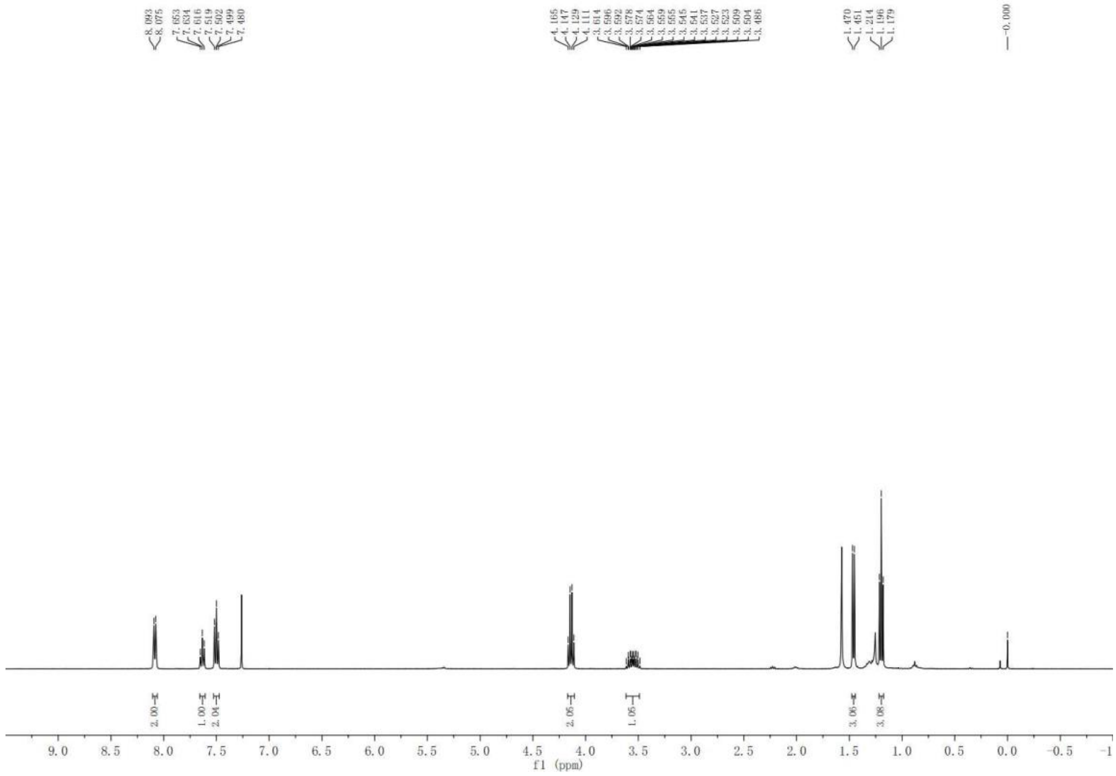
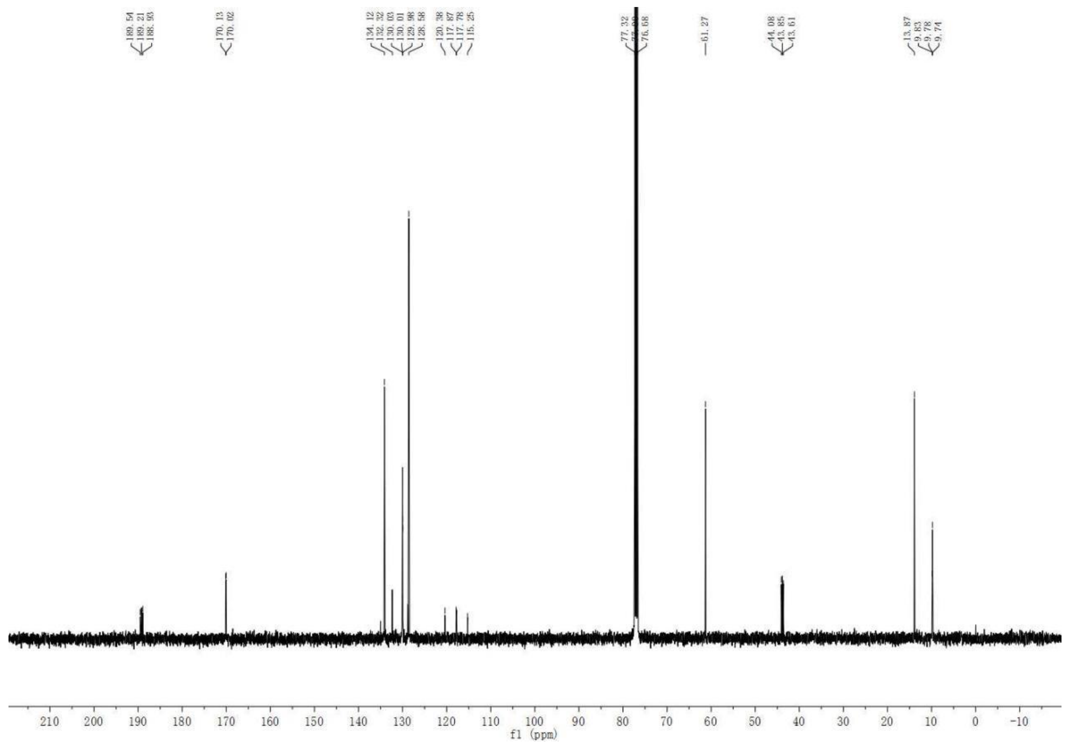
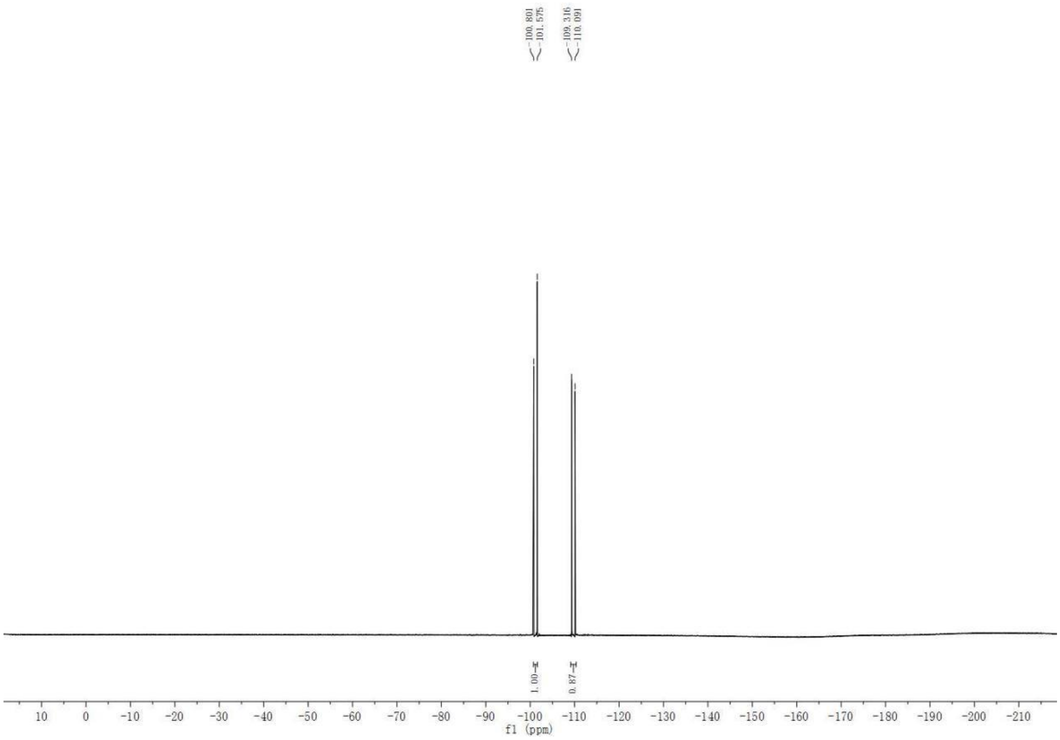
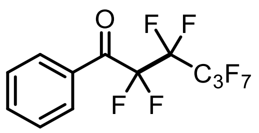





-100.801
-101.575
-109.316
-110.091
1.00
0.87
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



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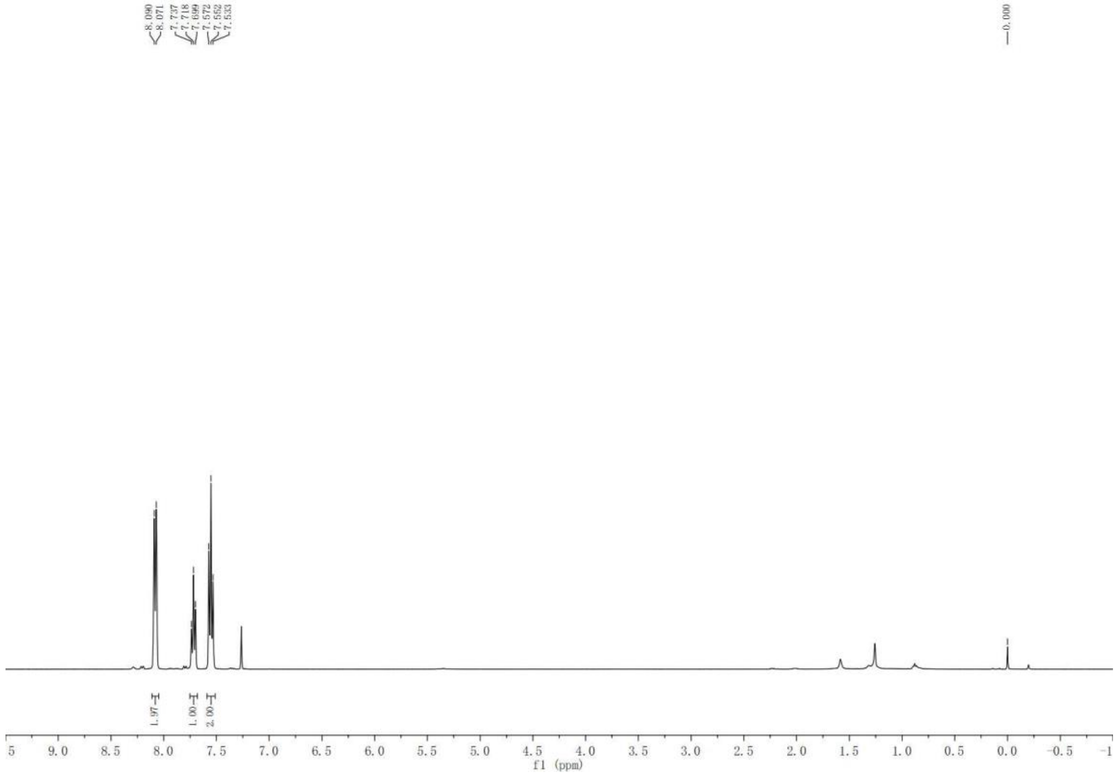
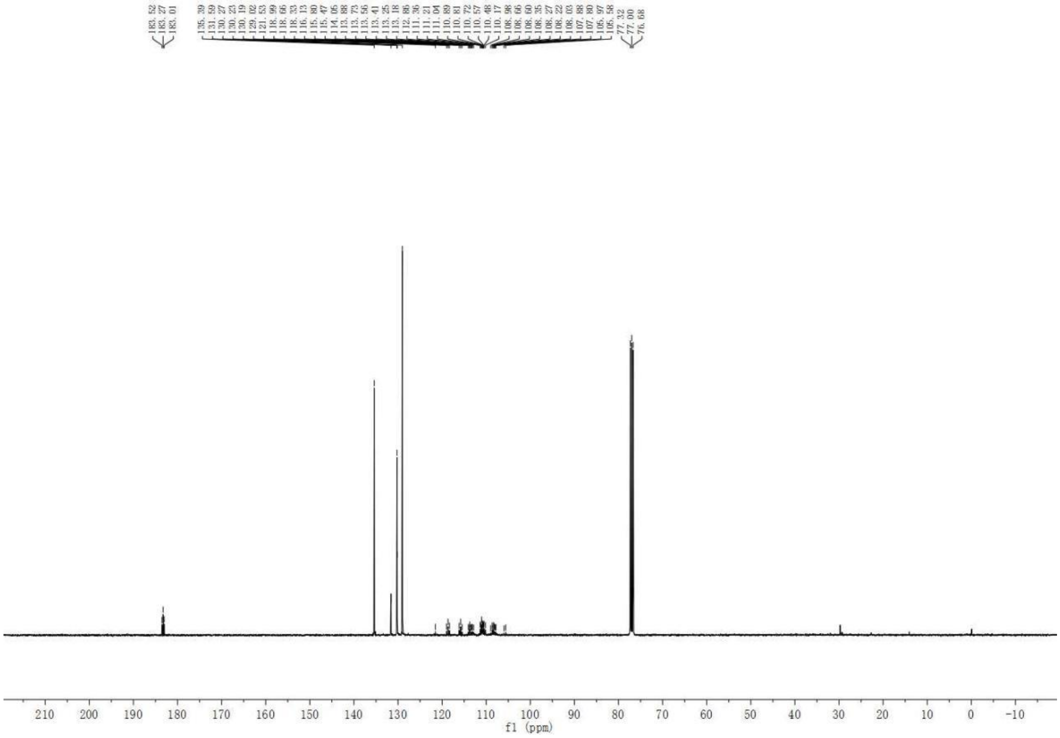
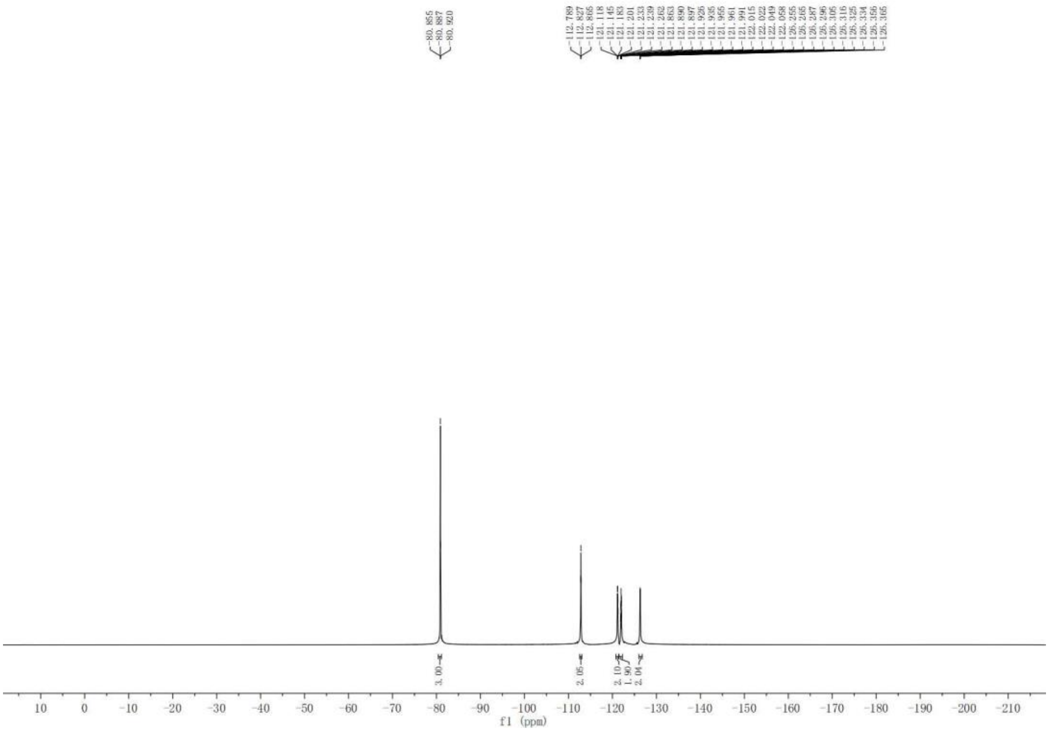
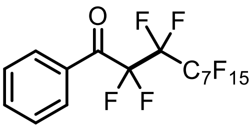
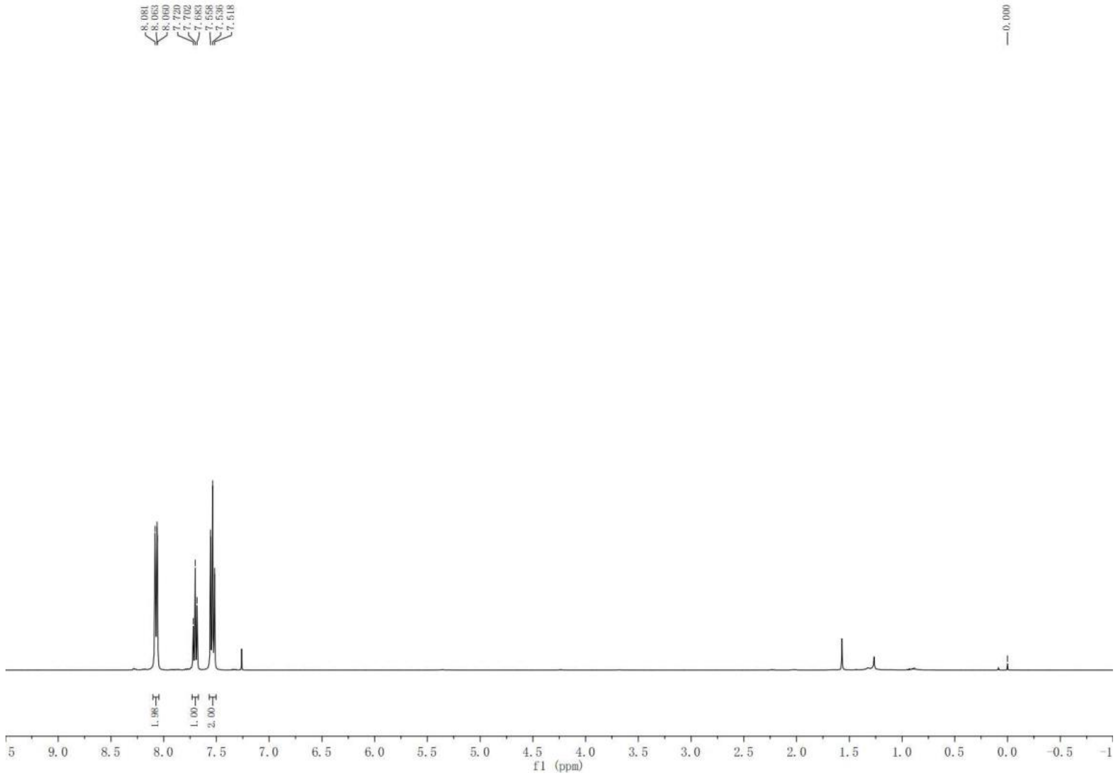








3la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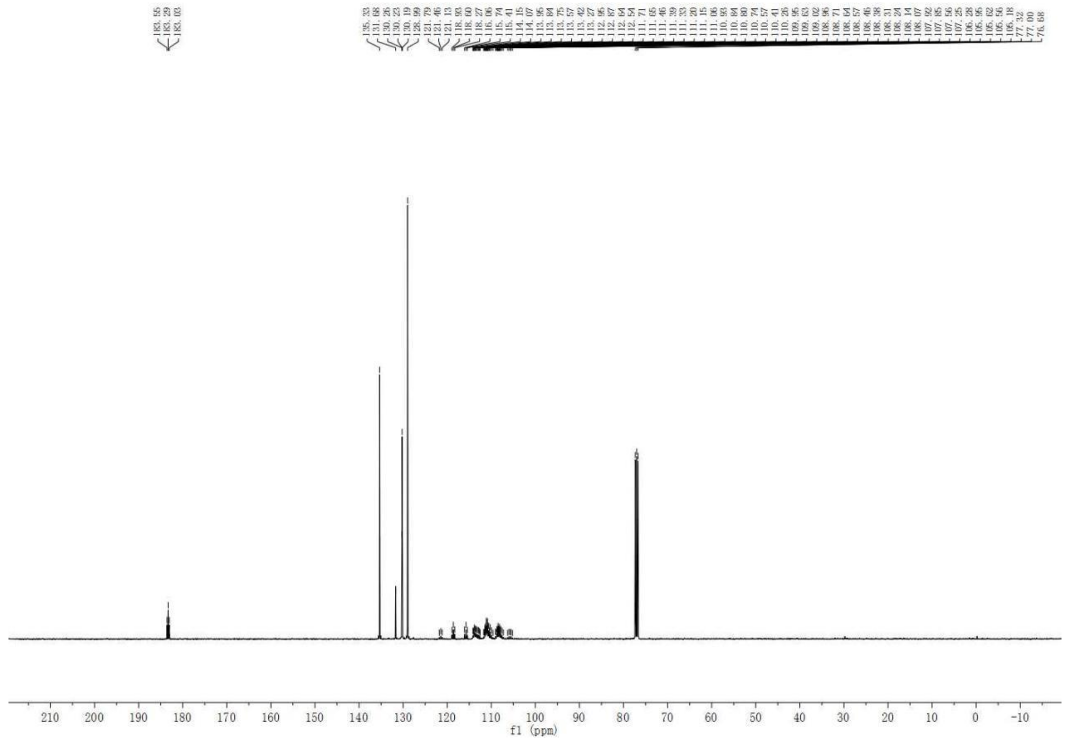
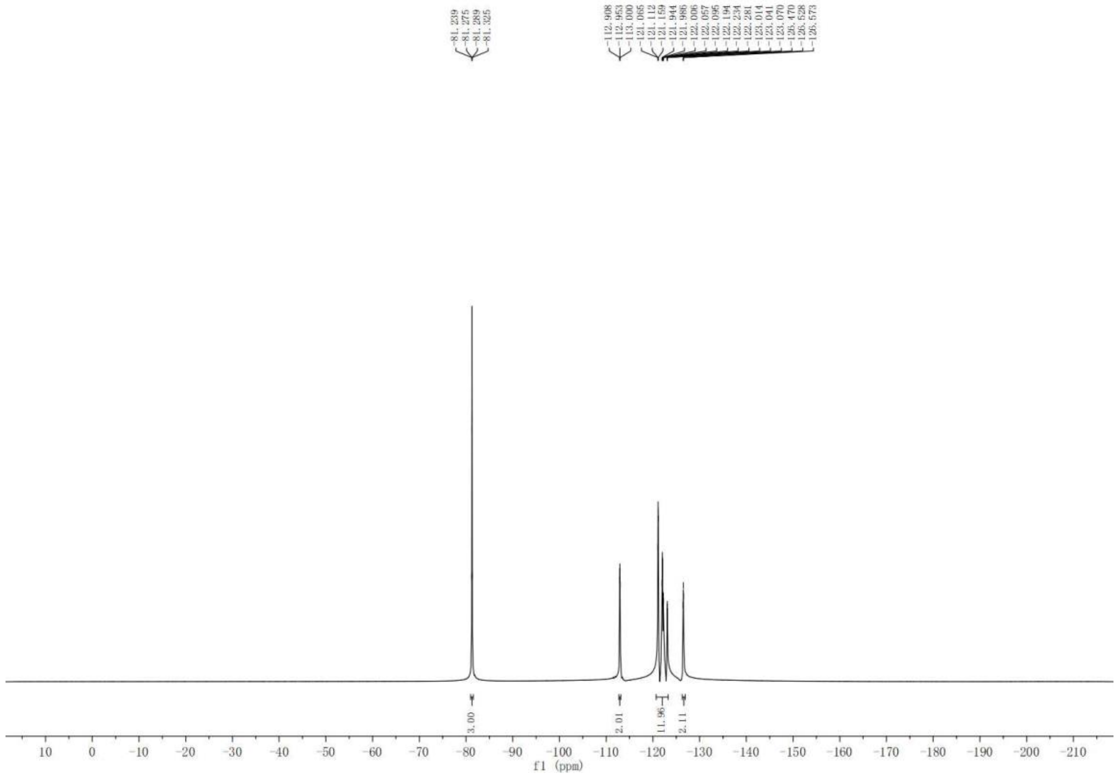
8.060
7.720
7.702
7.683
7.558
7.536
7.518
0.000
1.98
1.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)





-81.239
-81.275
-81.289
-81.325
-112.908
-112.953
-113.000
-121.065
-121.112
-121.159
-121.944
-121.986
-122.006
-122.057
-122.095
-122.194
-122.234
-122.281
-123.014
-123.041
-123.070
-126.470
-126.528
-126.573
3.00
2.01
11.96
2.11
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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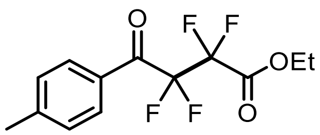
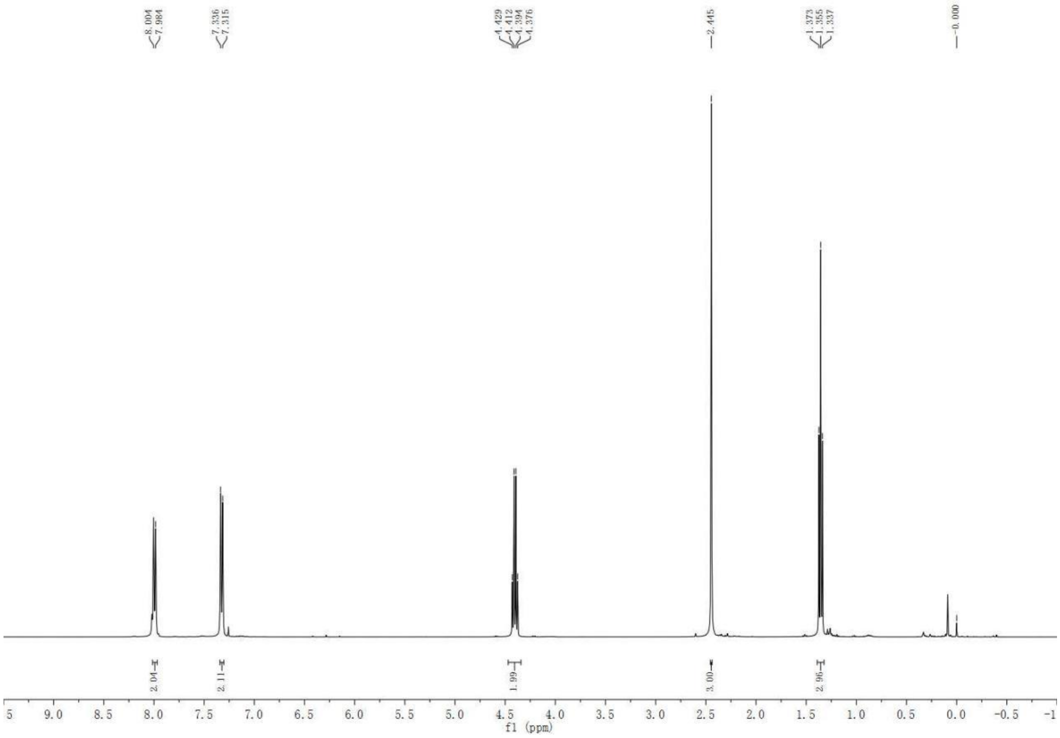
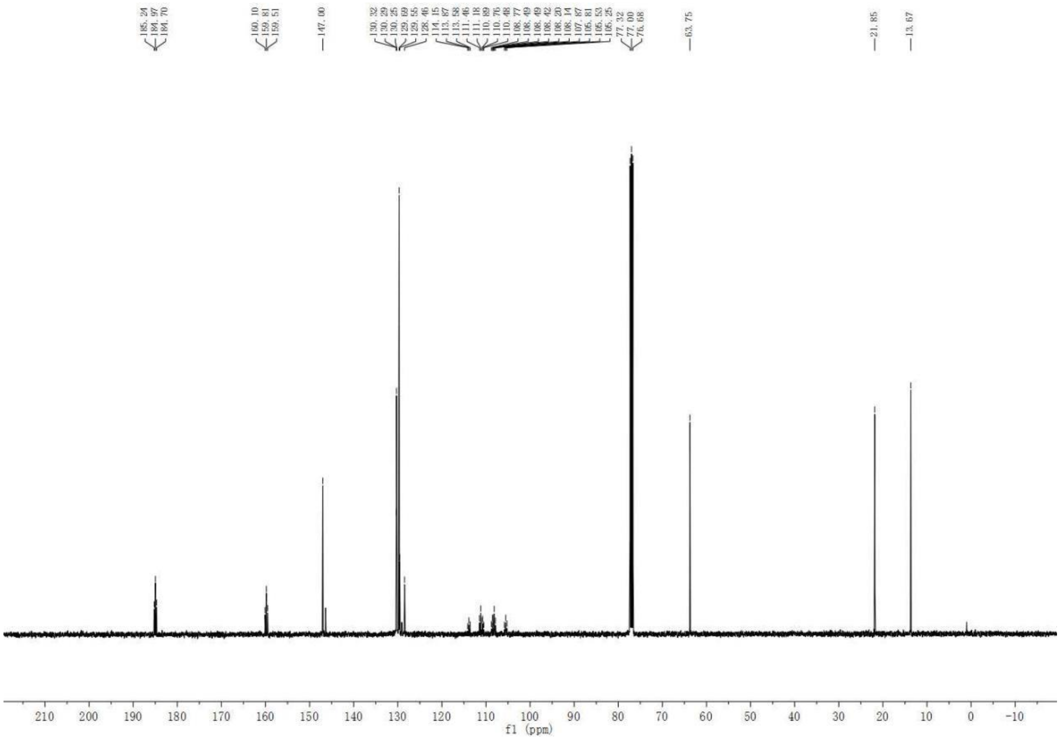
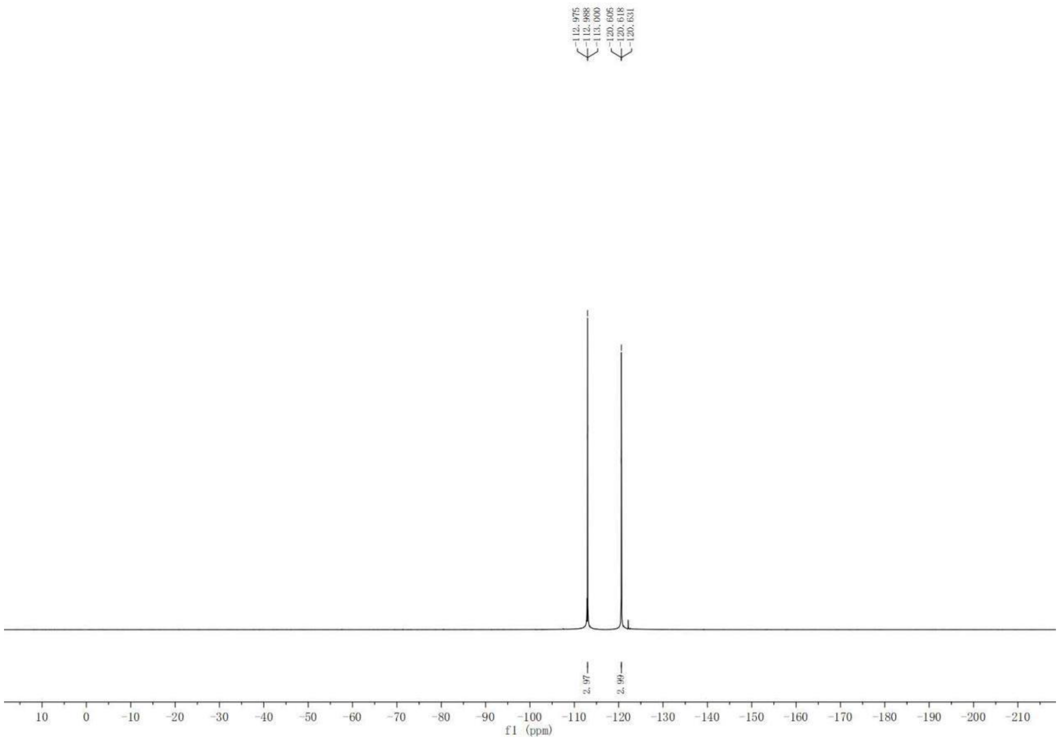
-200
-210
f1 (ppm)


O
F
F
OEt
F
F
O

3ab


8.004
7.984
7.336
7.315
4.429
4.412
4.394
4.376
2.445
1.373
1.355
1.337
0.000
2.04
2.11
1.99
3.00
2.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


185.24
184.97
184.70
160.10
159.81
159.51
147.00
130.32
130.29
130.25
129.69
129.55
128.46
114.15
113.87
113.58
111.46
111.18
110.89
110.76
110.48
108.77
108.49
108.49
108.42
108.20
108.14
107.87
105.81
105.53
105.25
77.32
77.00
76.68
63.75
21.85
13.67
f1 (ppm)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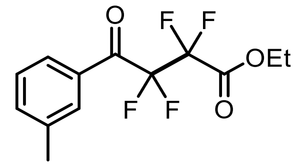
-113.000
-120.605
-120.618
-120.631
2.97
2.99
f1 (ppm)



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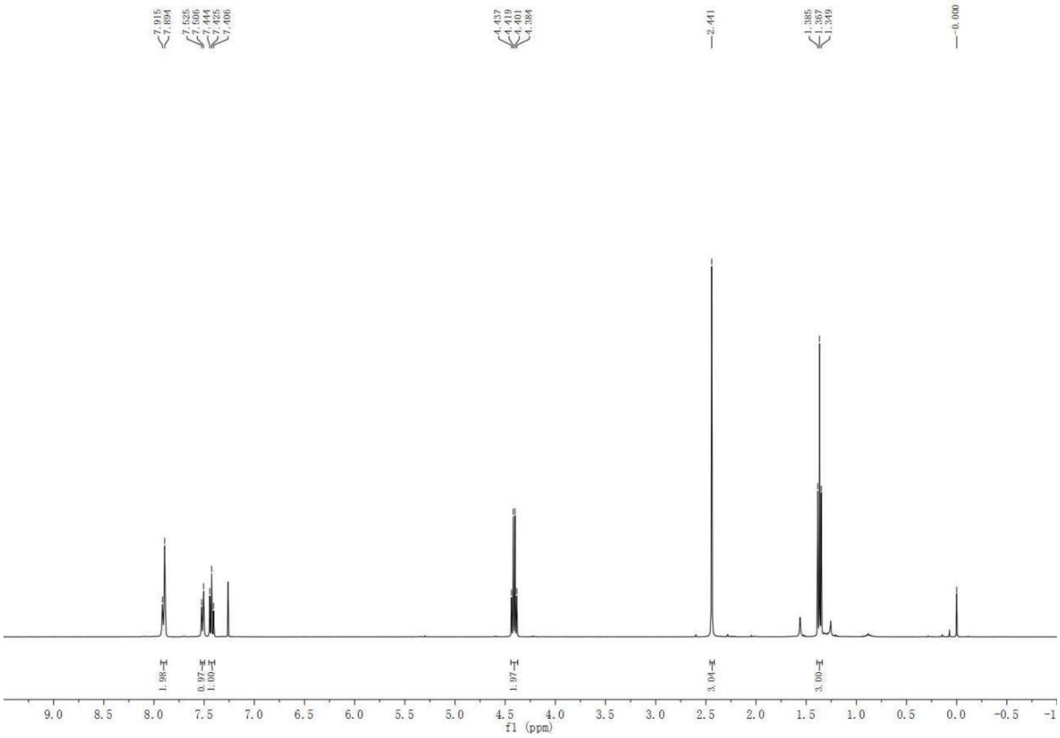

7.915
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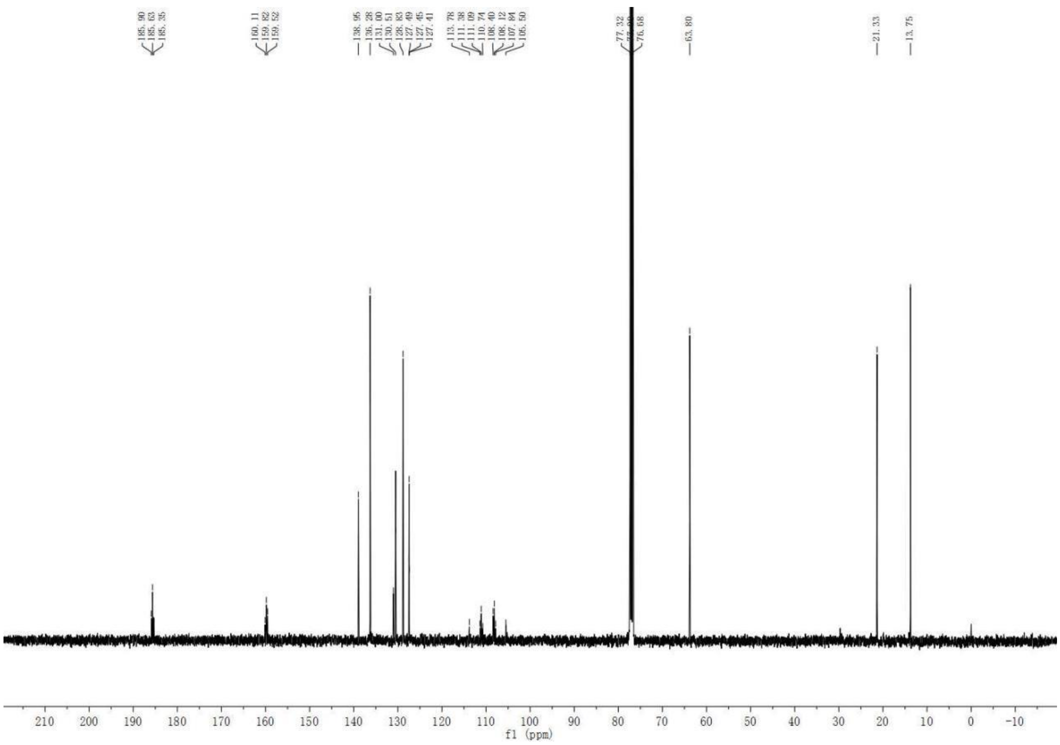
7.525
7.506
7.444
7.425
7.406
4.437
4.419
4.401
4.384
2.441
1.385
1.367
1.349
0.000
1.98
0.97
1.00
1.97
3.04
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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185.63
185.35
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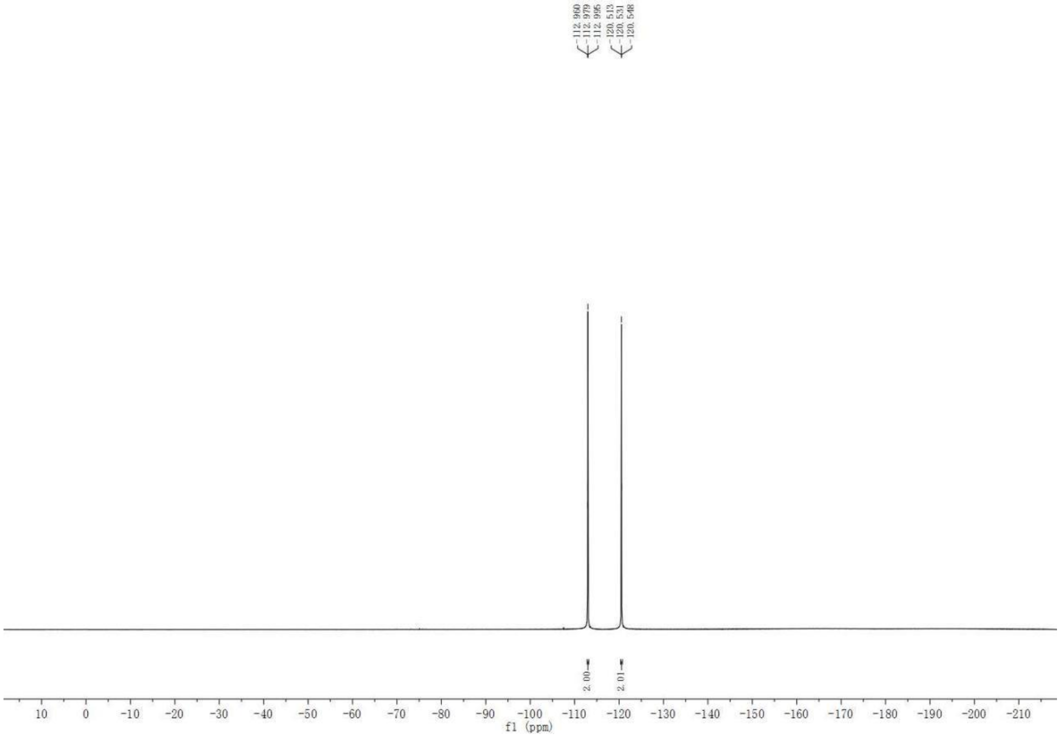
136.28
131.00
130.51
128.83
127.49
127.45
127.41
113.78
111.38
111.09
110.74
108.40
108.12
107.84
105.50
77.32
76.68
63.80
21.33
13.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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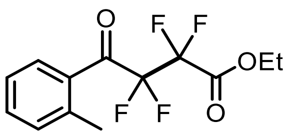
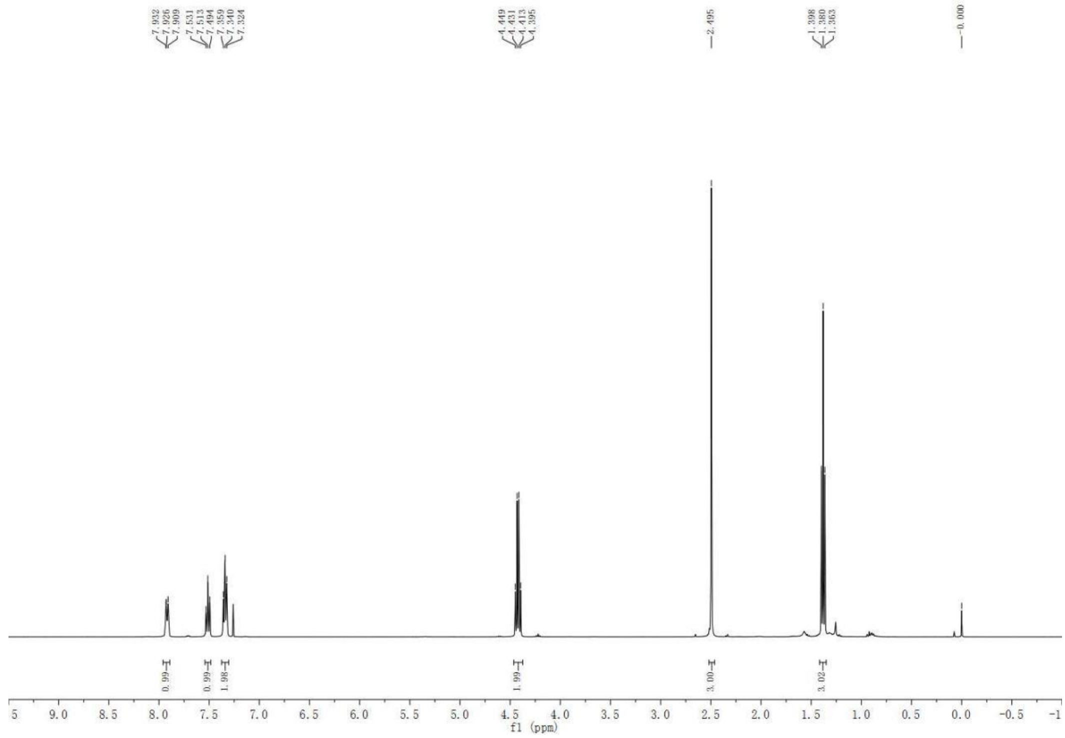
-120.513
-120.531
-120.548
2.00
2.01
f1 (ppm)



3ad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7.909
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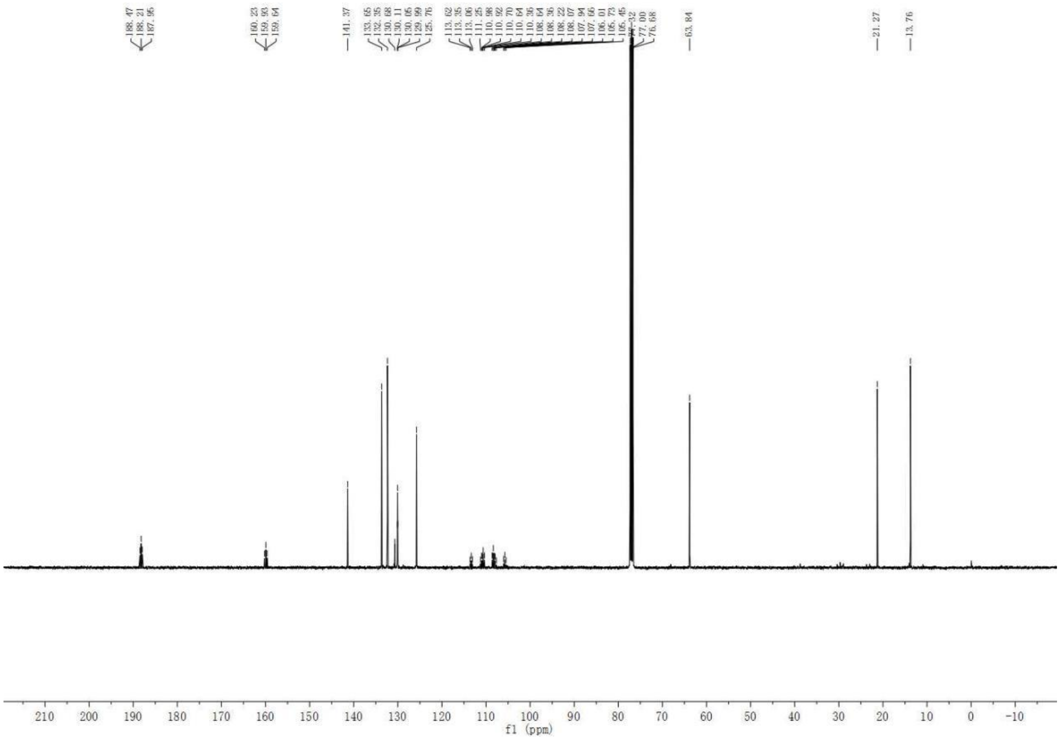
7.359
7.340
7.324
4.449
4.431
4.413
4.395
2.495
1.398
1.380
1.363
0.000
0.99
0.99
1.98
1.99
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



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188.21
187.95
160.23
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159.64
141.37
133.65
132.35
130.68
130.11
130.05
129.99
125.76
113.62
113.35
113.06
111.25
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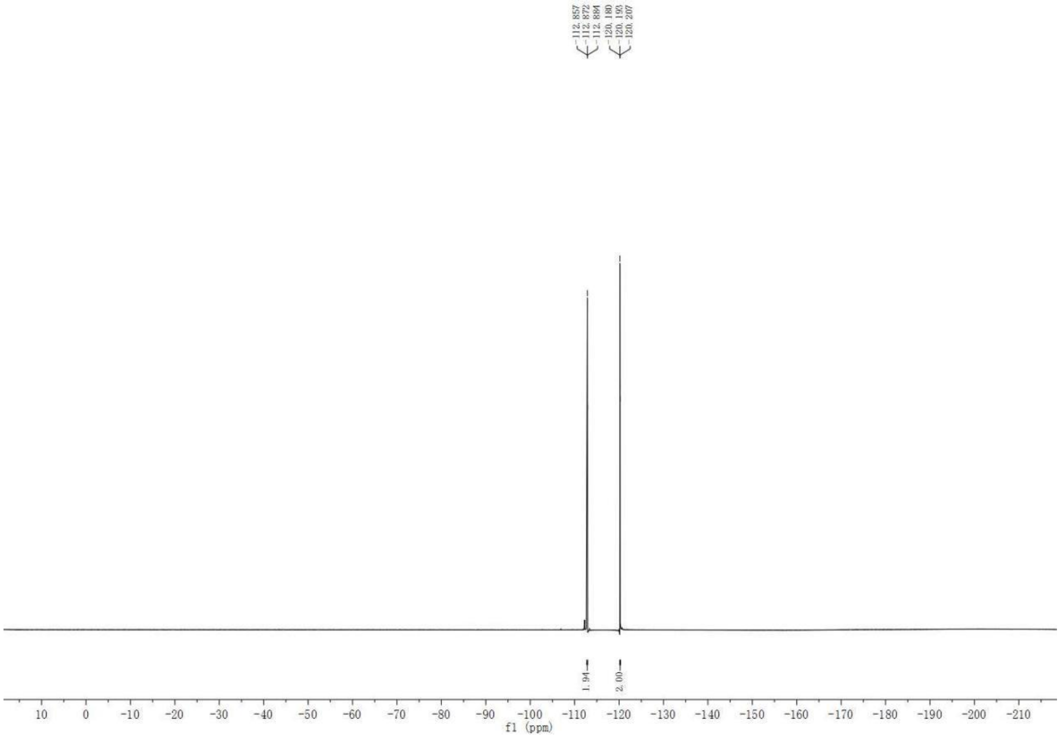
110.92
110.70
110.64
110.36
108.64
108.36
108.22
108.07
107.94
107.66
106.01
105.73
105.45
77.32
77.00
76.68
63.84
21.27
13.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.00
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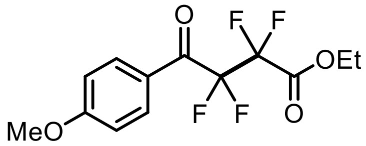
f1 (ppm)



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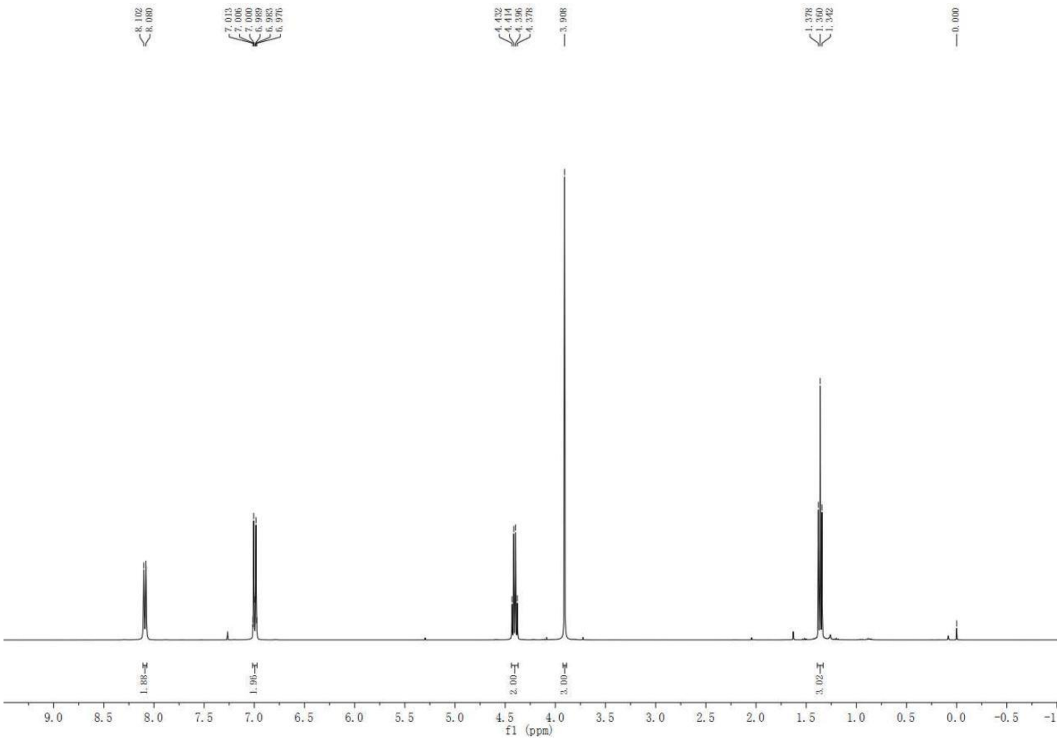

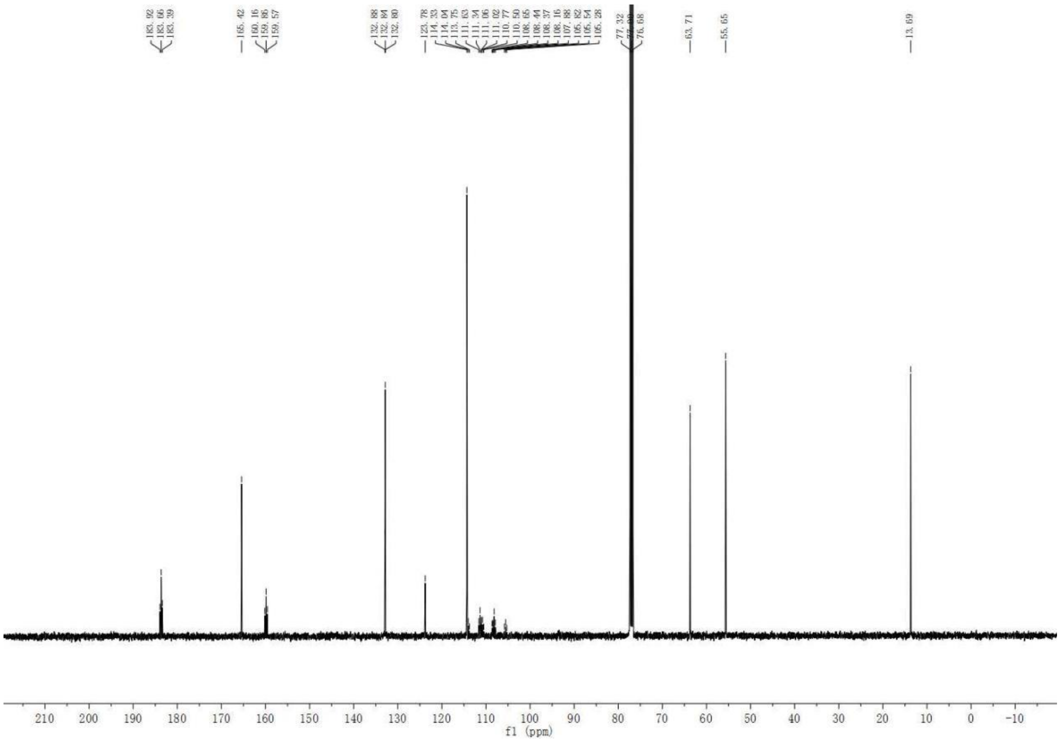

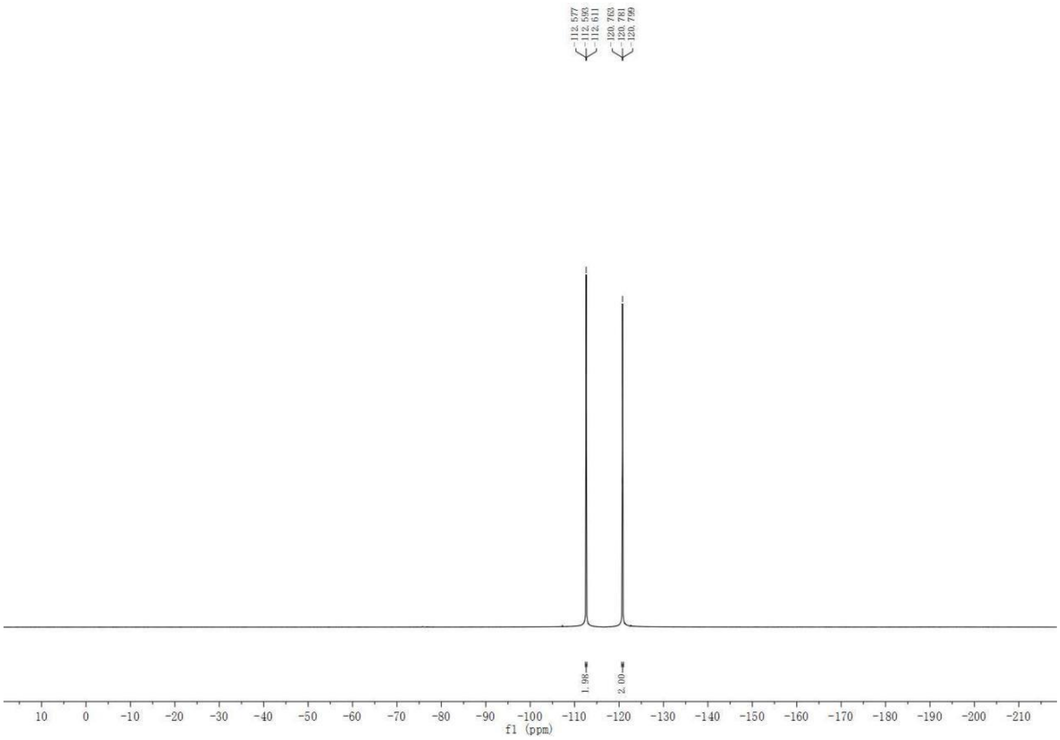
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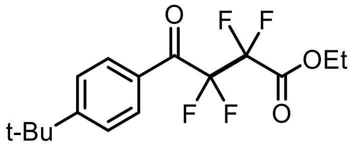
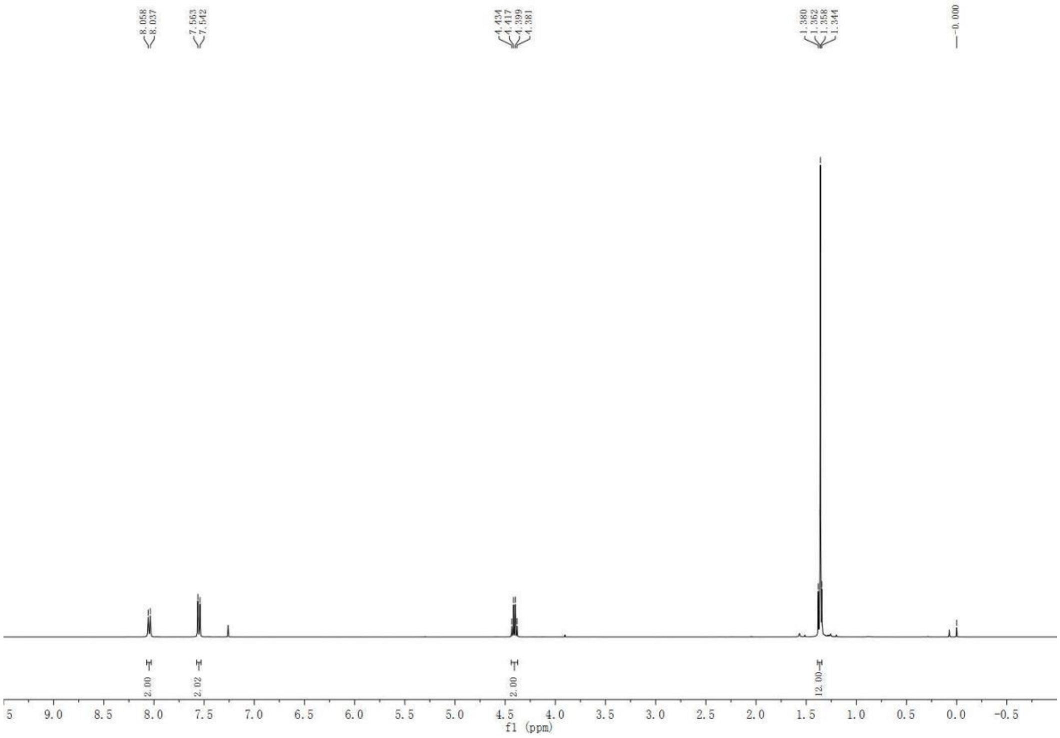
-120.763
-120.781
-120.799
1.98
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


O
F
F
OEt
t-Bu
F
F
O

3af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7.563
7.542
4.434
4.417
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4.381
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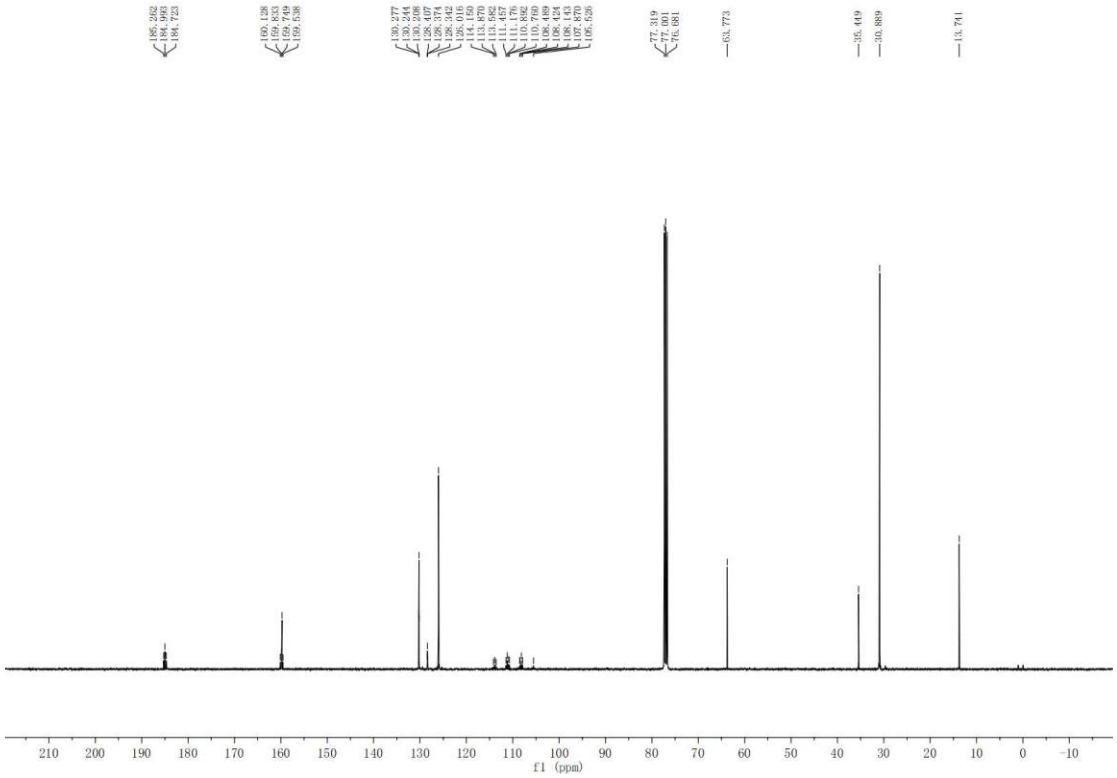
1.362
1.358
1.344
0.000
2.00
2.02
2.00
12.00
f1 (ppm)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128.342
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114.150
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111.176
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110.760
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105.526
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77.001
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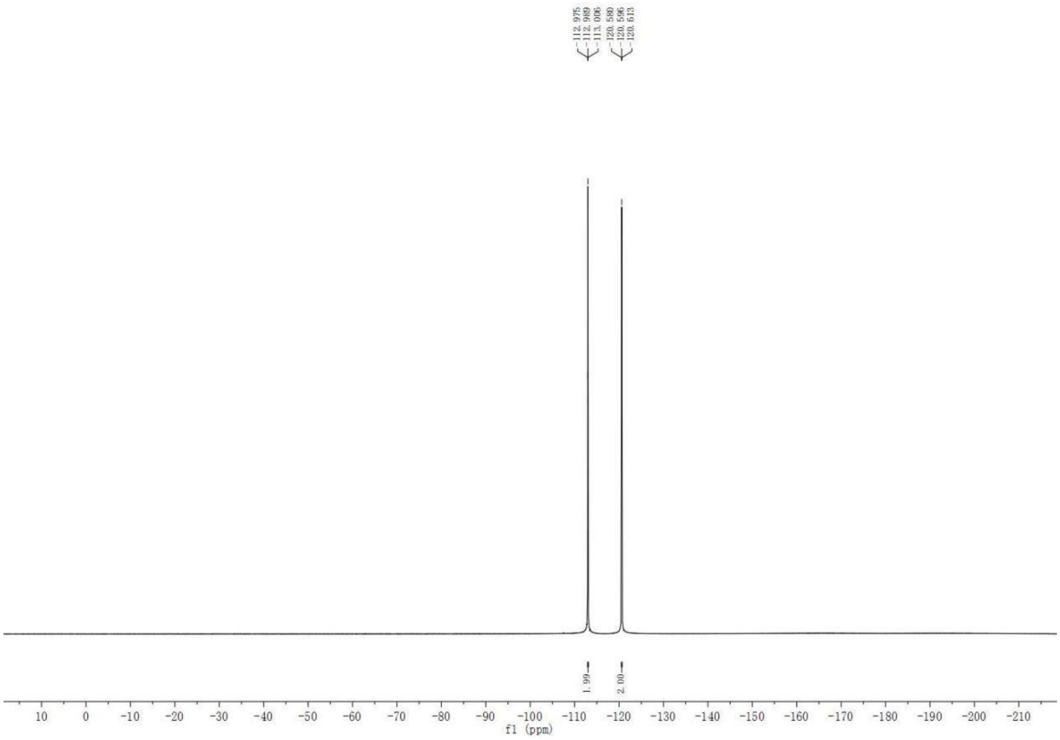
35.449
30.889
13.741
f1 (ppm)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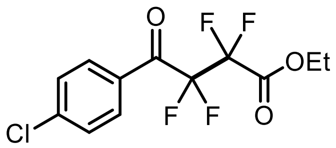
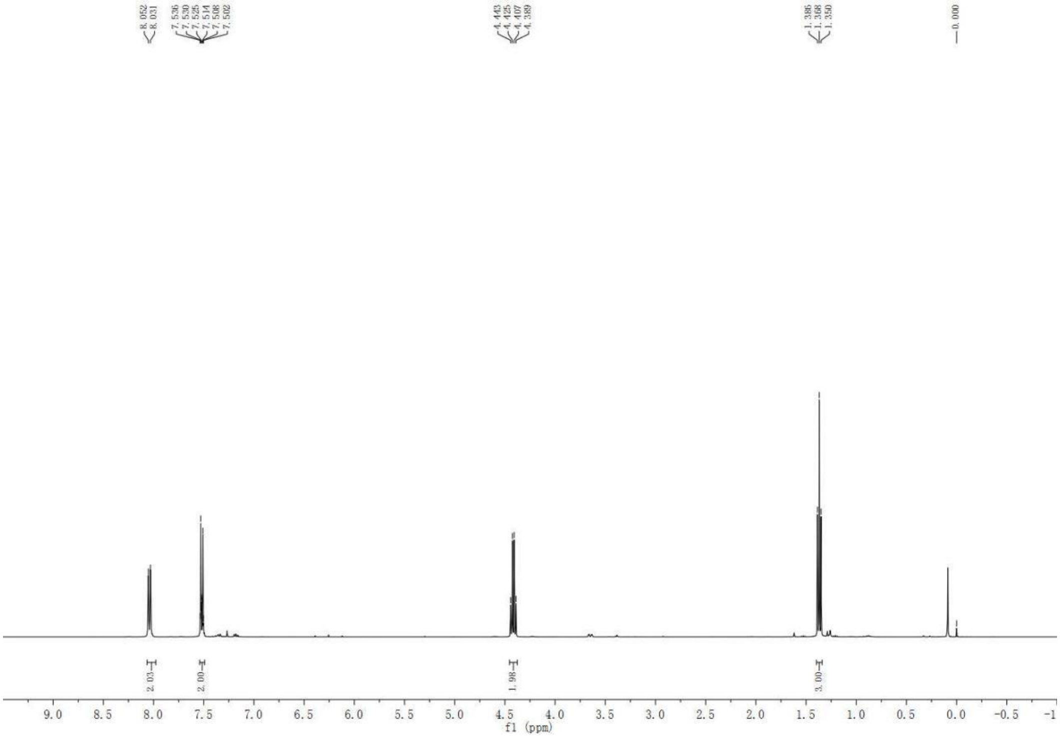
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



3ag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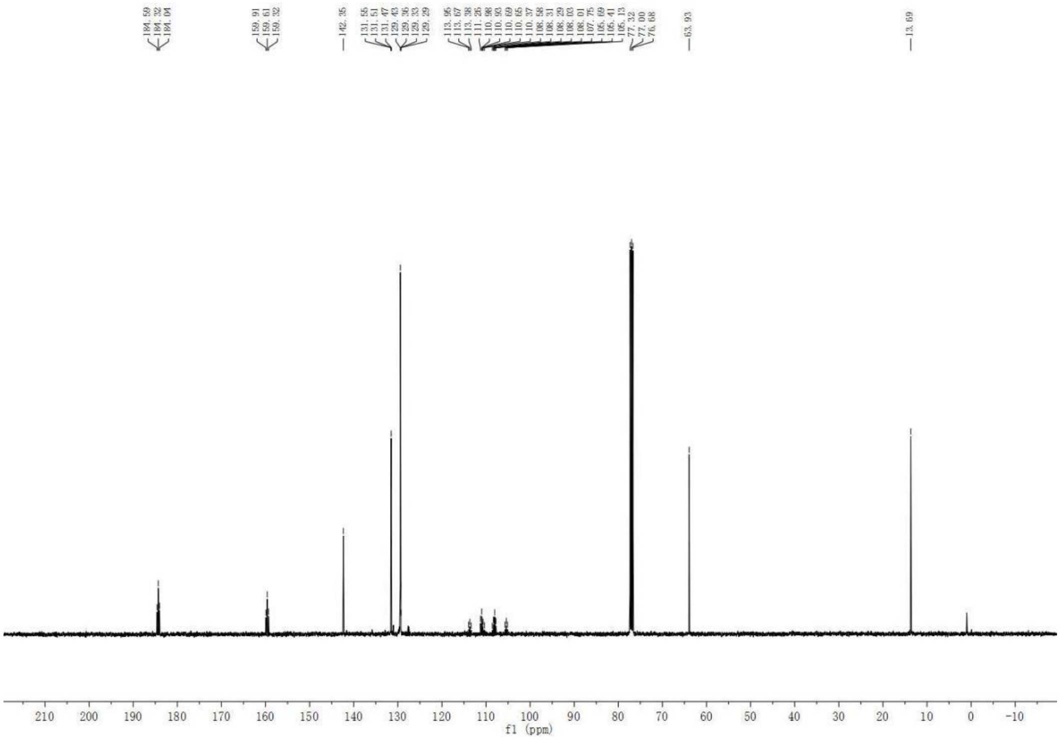
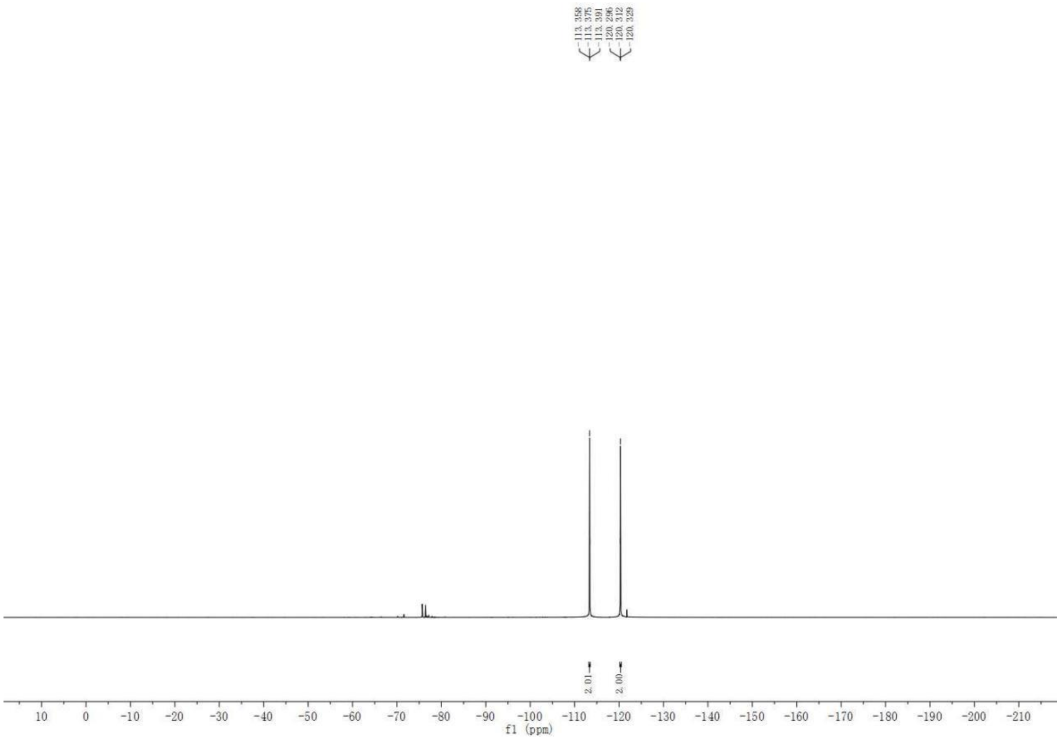
7.536
7.530
7.525
7.514
7.508
7.502
4.443
4.425
4.407
4.389
1.386
1.368
1.350
0.000
2.03
2.00
1.98
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

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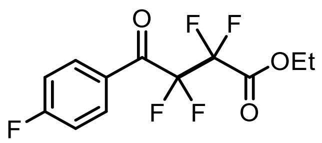
2.01
2.00
f1 (ppm)



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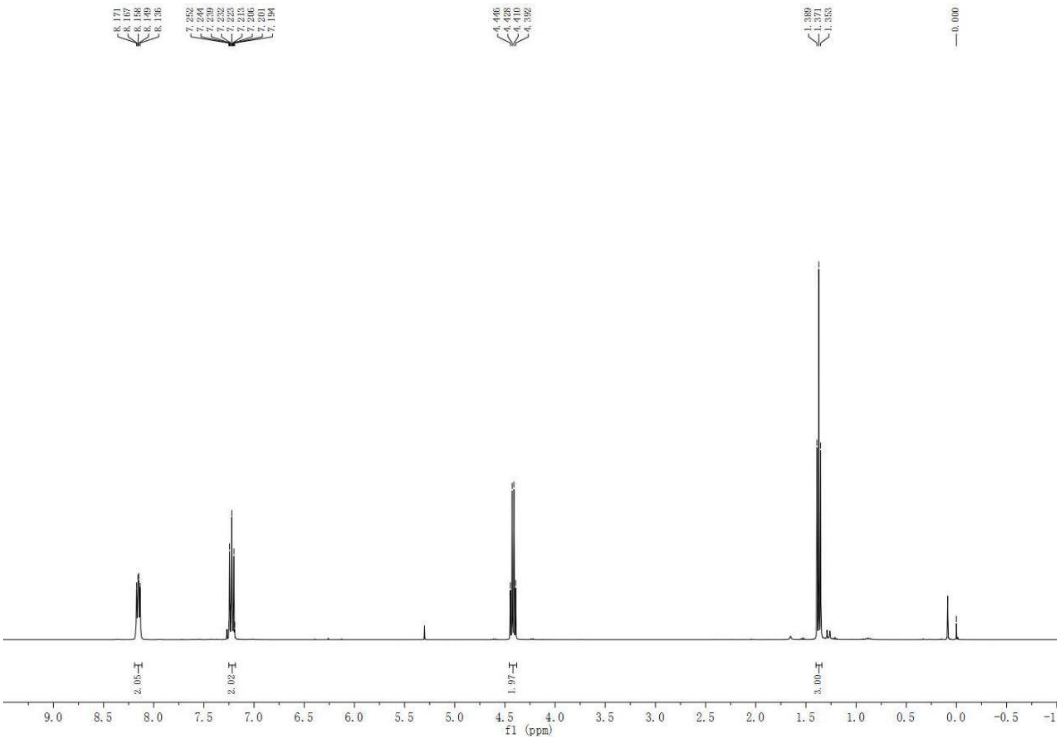
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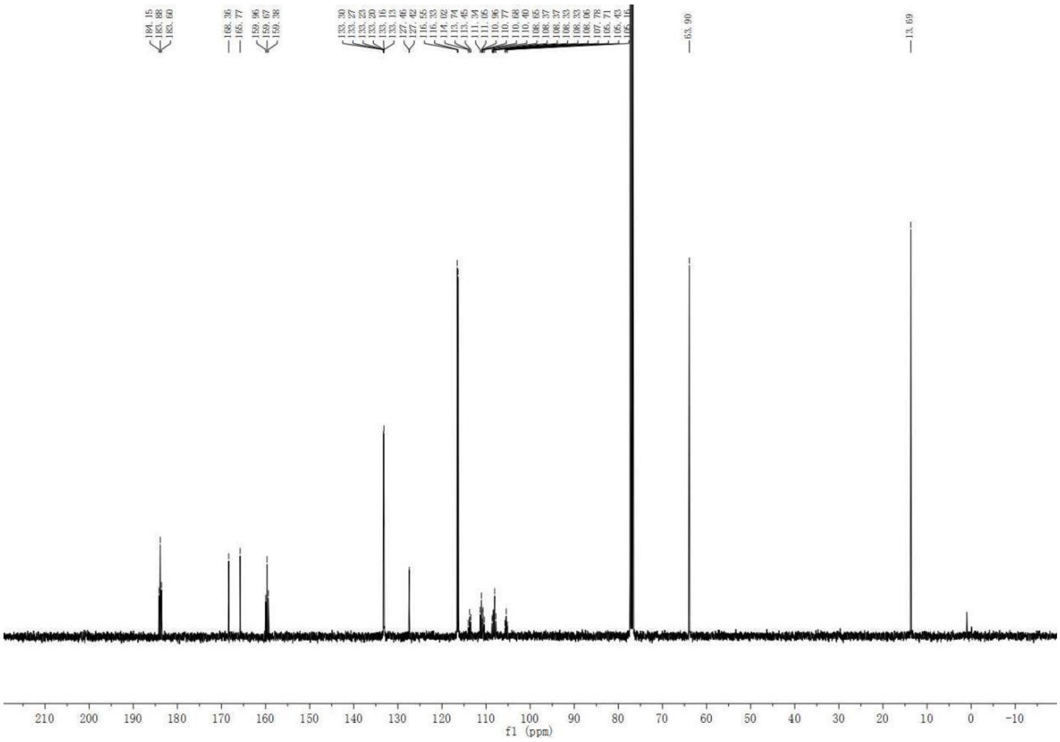
7.244
7.239
7.232
7.223
7.213
7.206
7.201
7.194
4.446
4.428
4.410
4.392
1.389
1.371
1.353
0.000
2.05
2.02
1.97
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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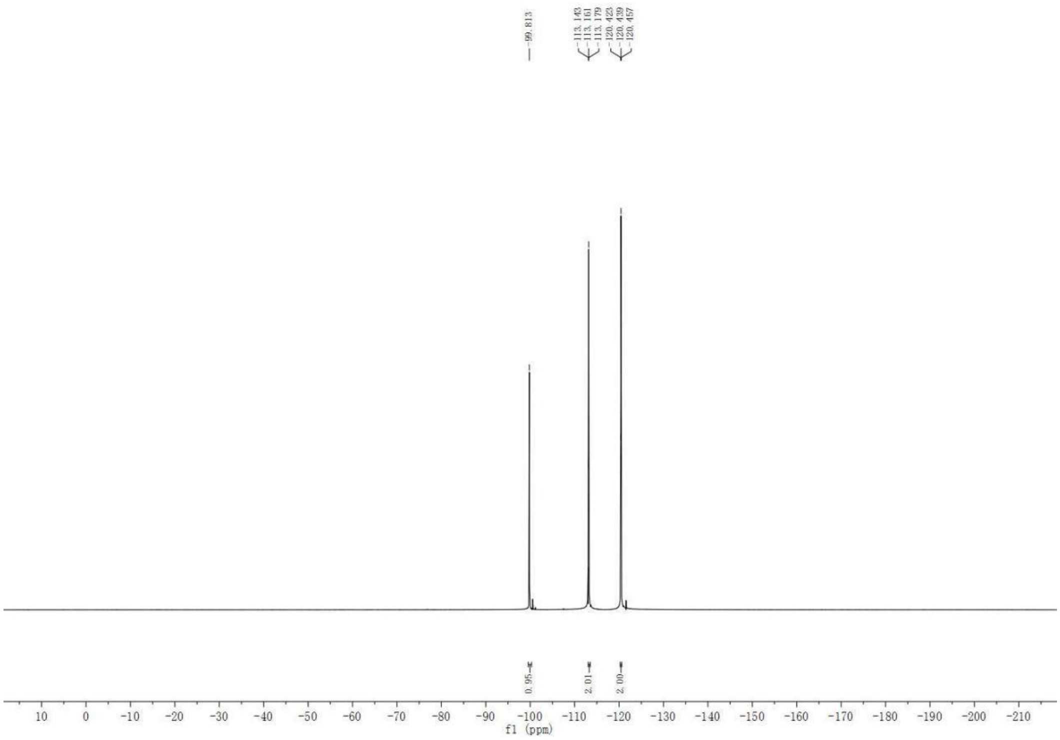
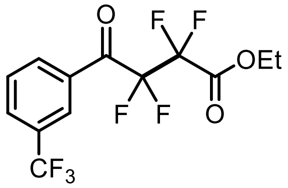
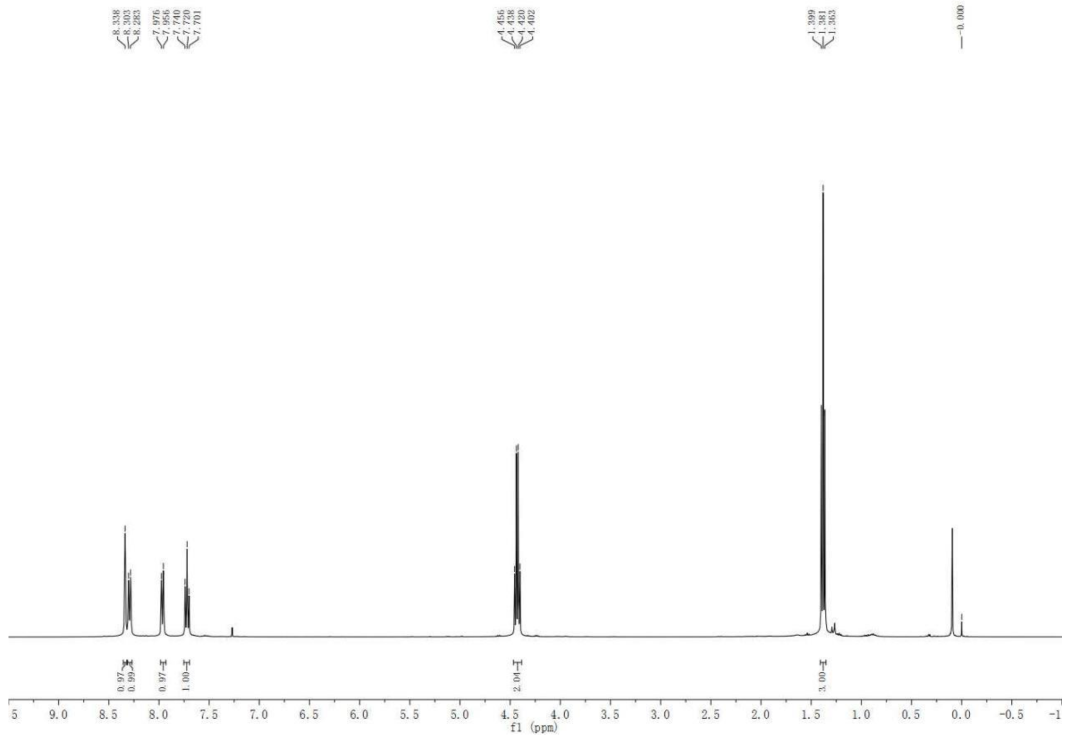
133.23
133.20
133.16
133.13
127.46
127.42
116.55
116.33
114.02
113.74
113.45
111.34
111.05
110.96
110.77
110.68
110.40
108.65
108.37
108.37
108.33
108.33
108.06
107.78
105.71
105.43
105.15
63.90
13.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



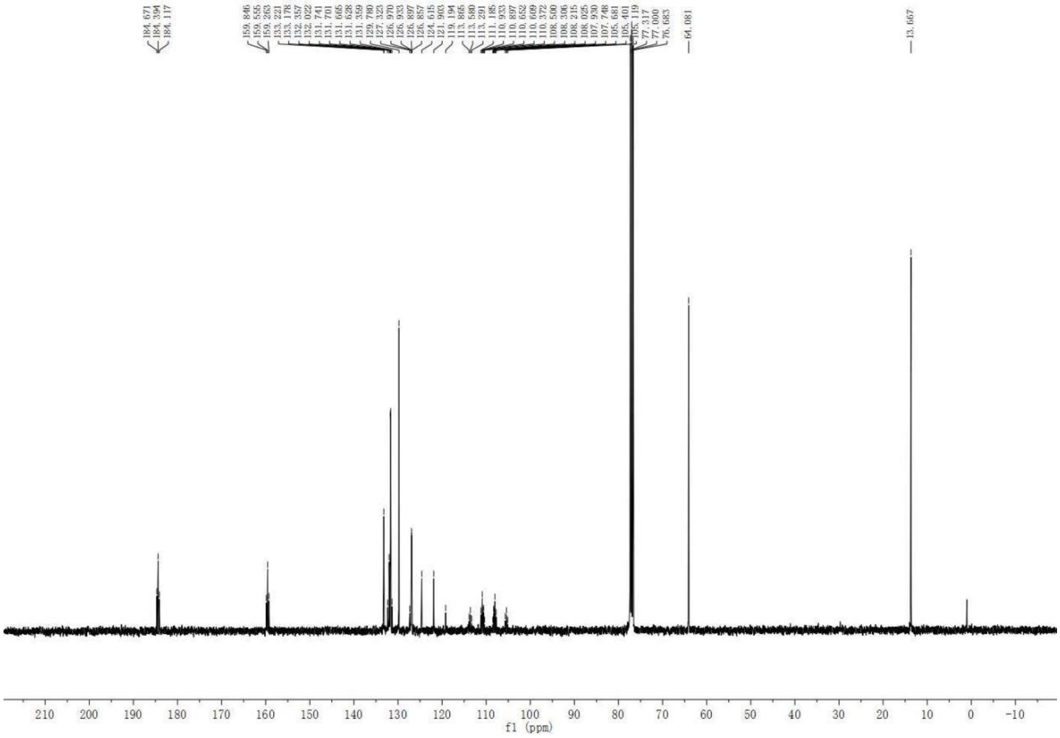
-99.813
-113.143
-113.161
-113.179
-120.423
-120.439
-120.457
0.95
2.01
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

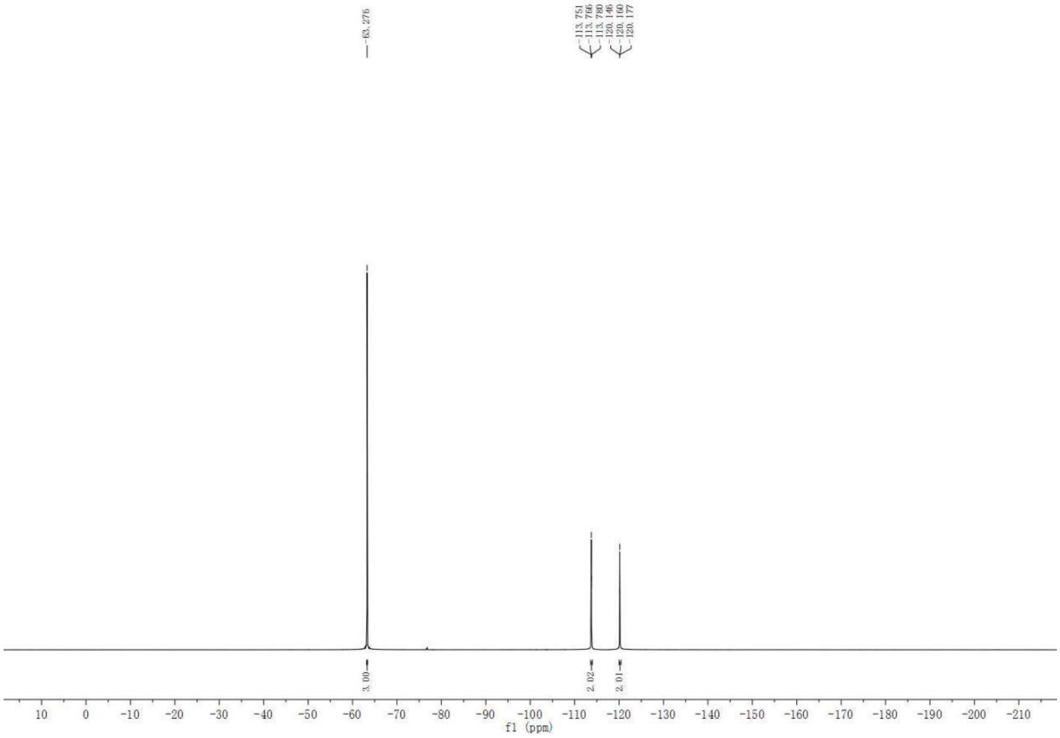


3ai

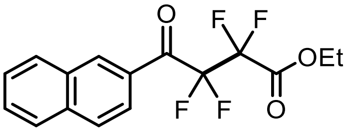


8.338
8.303
8.283
7.976
7.956
7.740
7.720
7.701
4.456
4.438
4.420
4.402
1.399
1.381
1.363
0.000
0.97
0.99
0.97
1.00
2.04
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

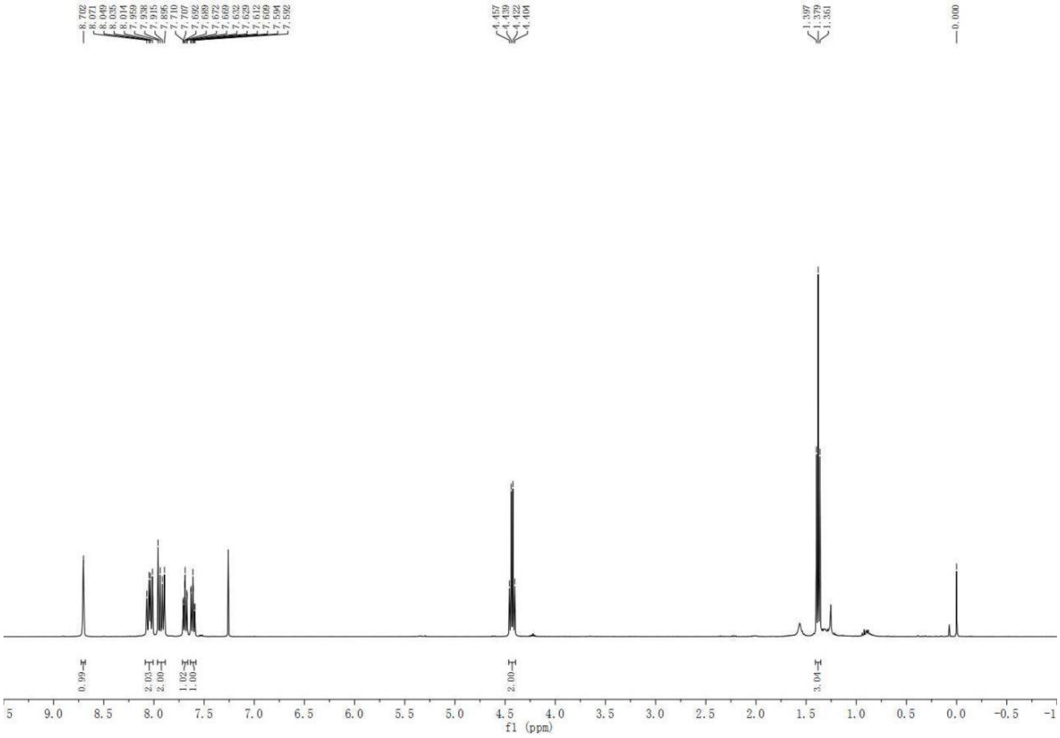


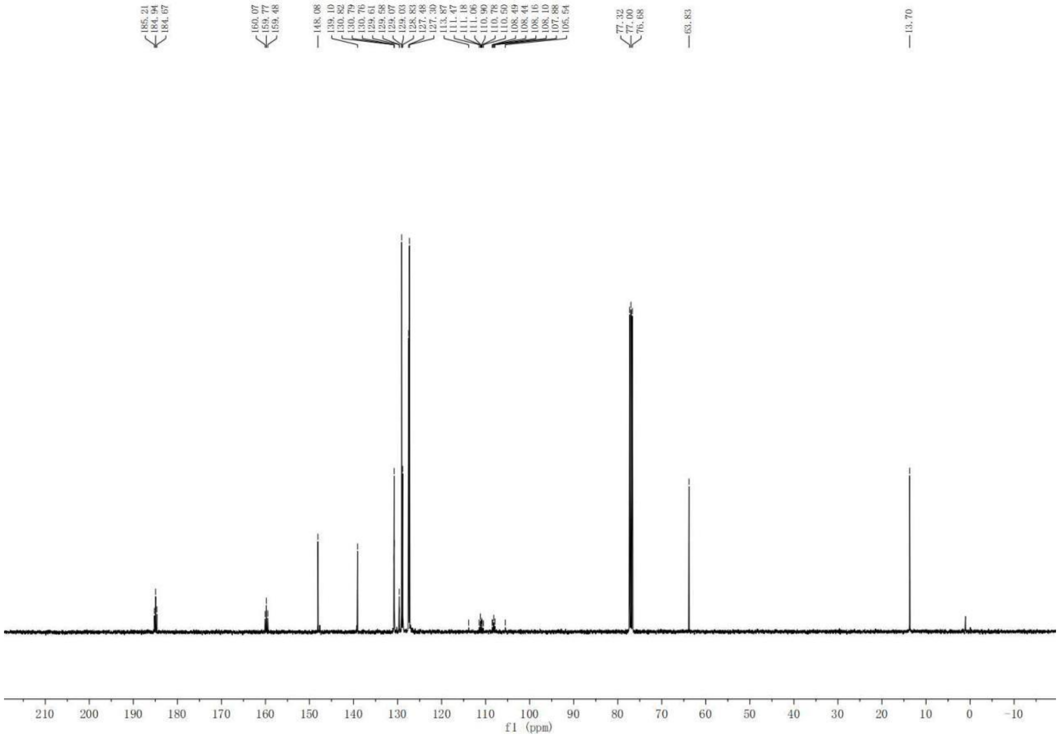


-63.276
-113.751
-113.766
-113.780
-120.146
-120.160
-120.177
3.00
2.02
2.01
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

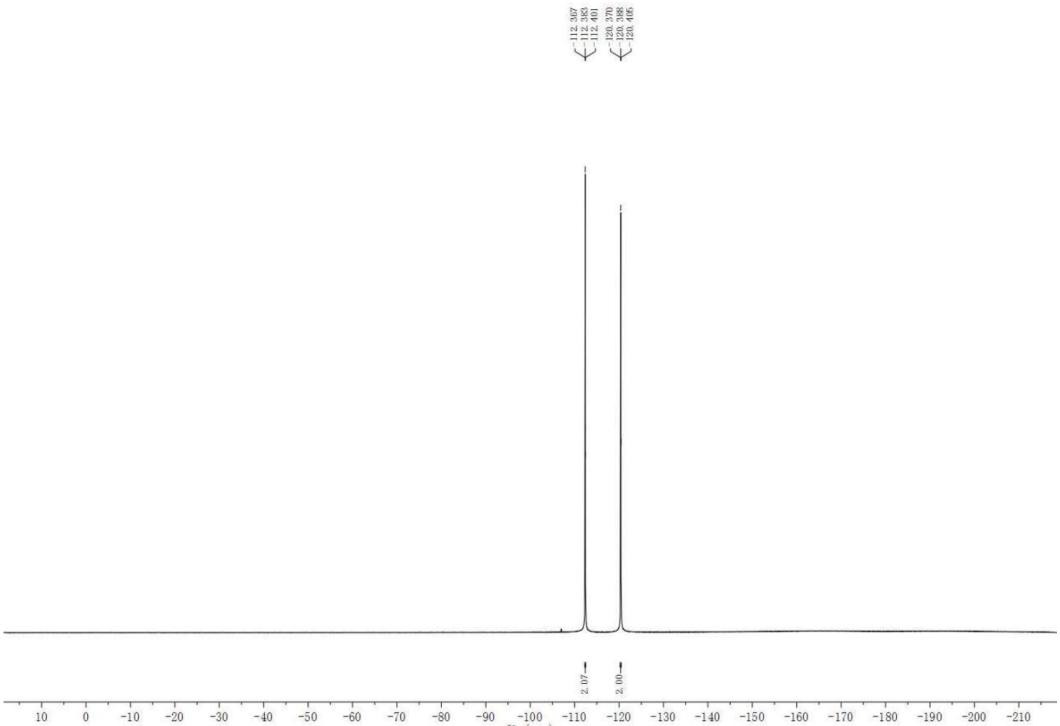


3aj





185.21
184.94
184.67
160.07
159.77
159.48
148.08
139.10
130.82
130.79
130.76
129.61
129.58
129.07
129.03
128.83
127.48
127.30
113.87
111.47
111.18
111.06
110.90
110.78
110.59
108.49
108.44
108.16
108.10
107.88
105.54
77.32
77.00
76.68
63.83
13.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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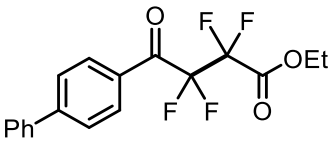
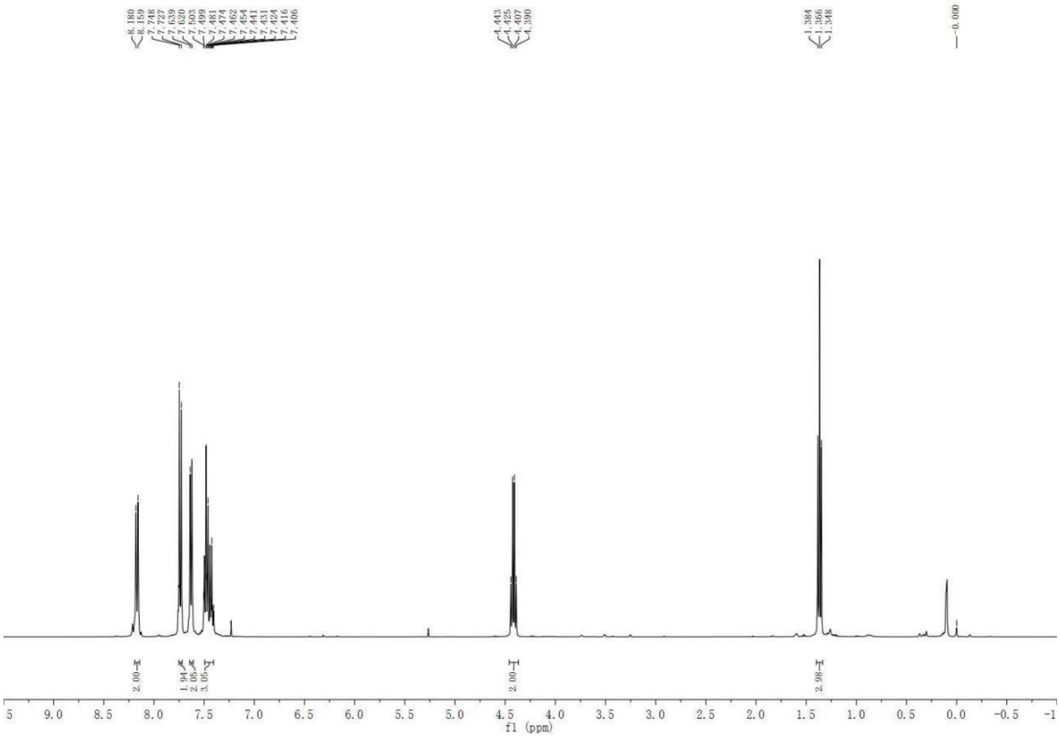
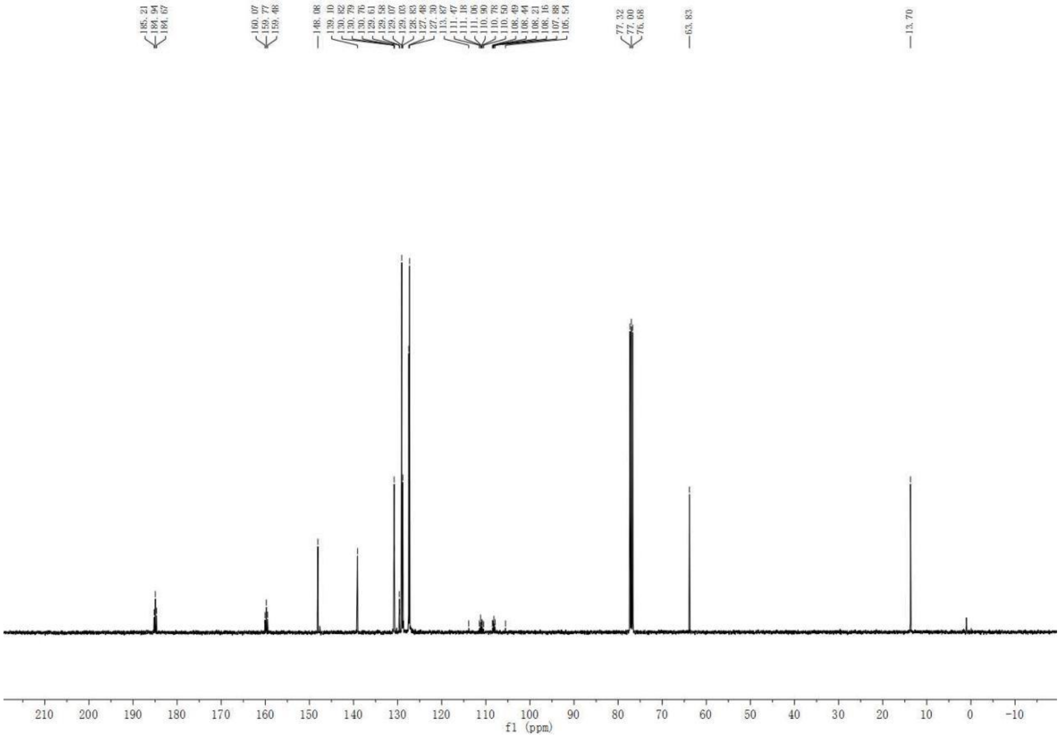
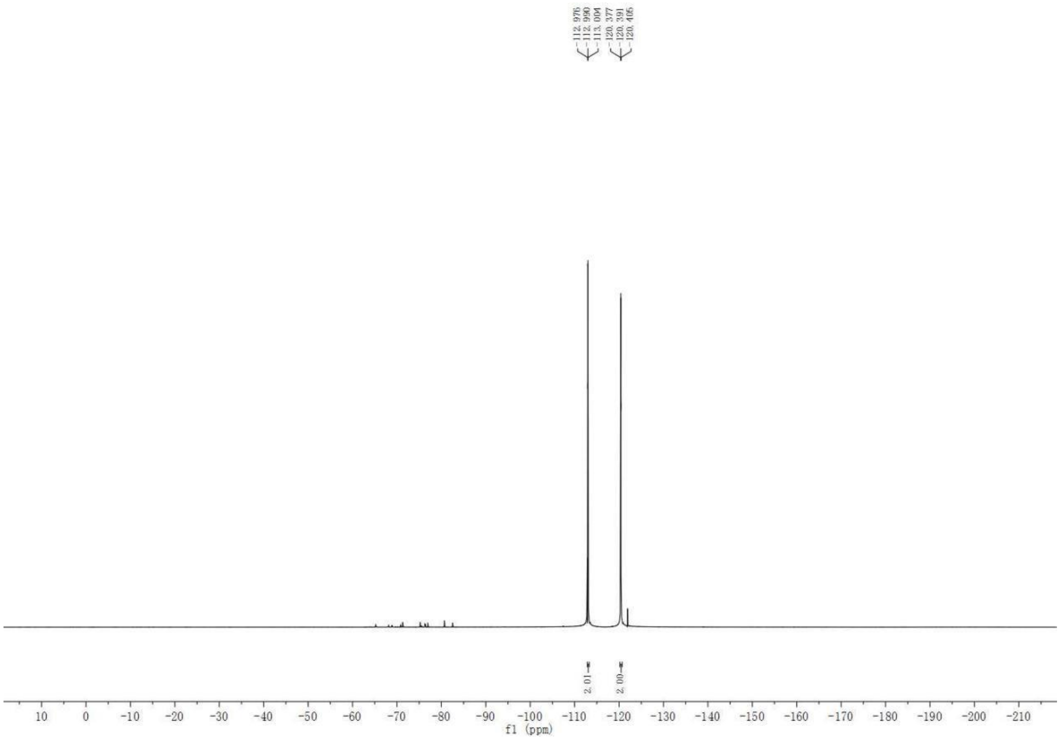
-112.383
-112.401
-120.370
-120.388
-120.405
2.07
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

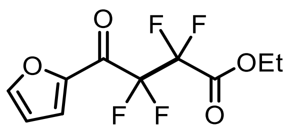

O
F
F
OEt
F
F
O
Ph

3ak

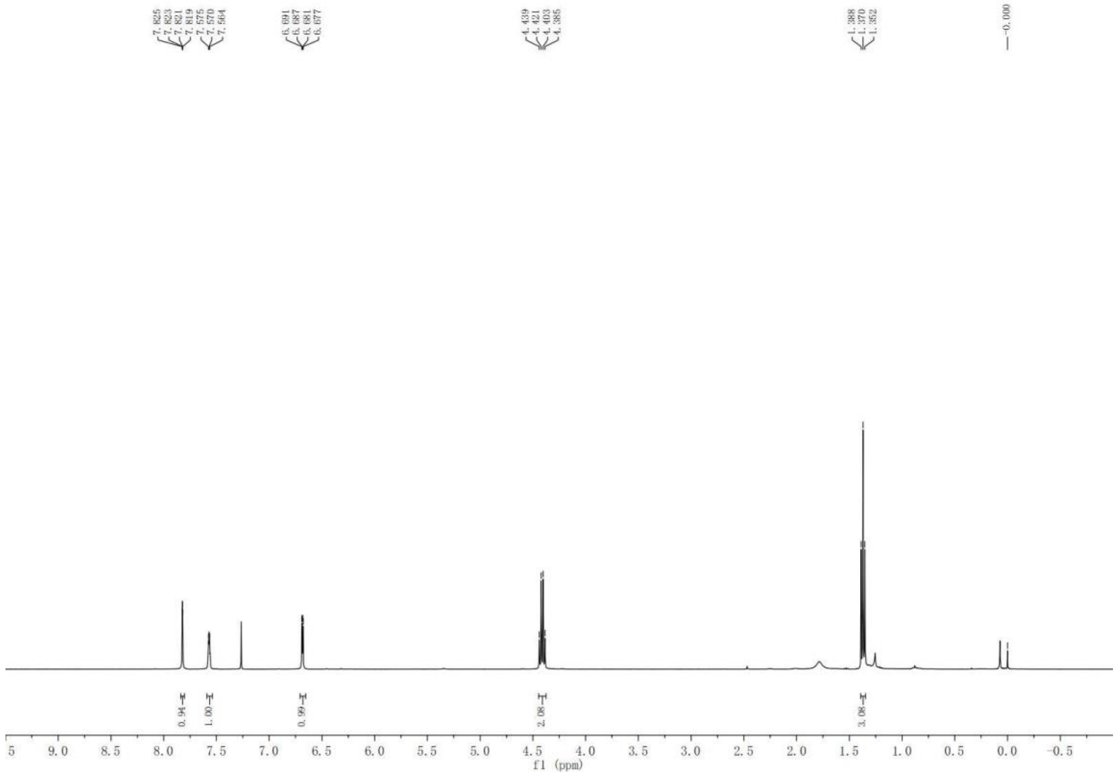

8.180
8.159
7.748
7.727
7.639
7.620
7.503
7.499
7.481
7.474
7.462
7.454
7.441
7.431
7.424
7.416
7.406
4.443
4.425
4.407
4.390
1.384
1.366
1.348
0.000
2.00
1.94
2.05
3.05
2.00
2.98
f1 (ppm)

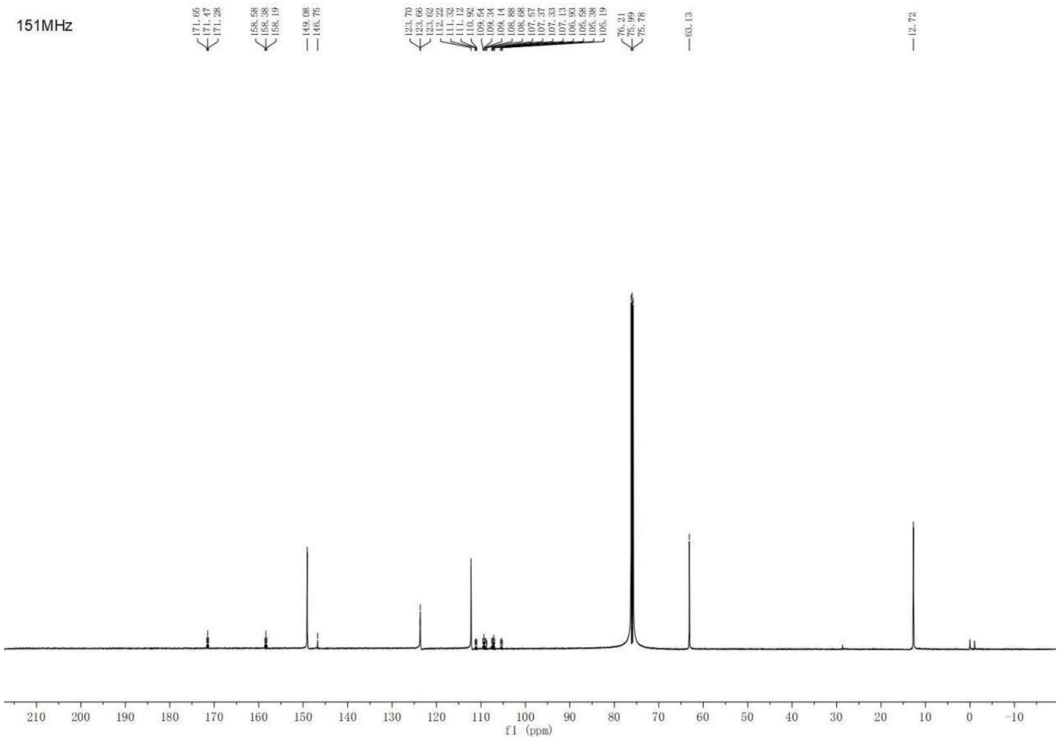

185.21
184.94
184.67
160.07
159.77
159.48
148.08
139.10
130.82
130.79
130.76
129.61
129.58
129.07
129.03
128.83
127.48
127.30
113.87
111.47
111.18
111.06
110.90
110.78
110.50
108.49
108.44
108.21
108.16
107.88
105.54
77.32
77.00
76.68
63.83
13.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

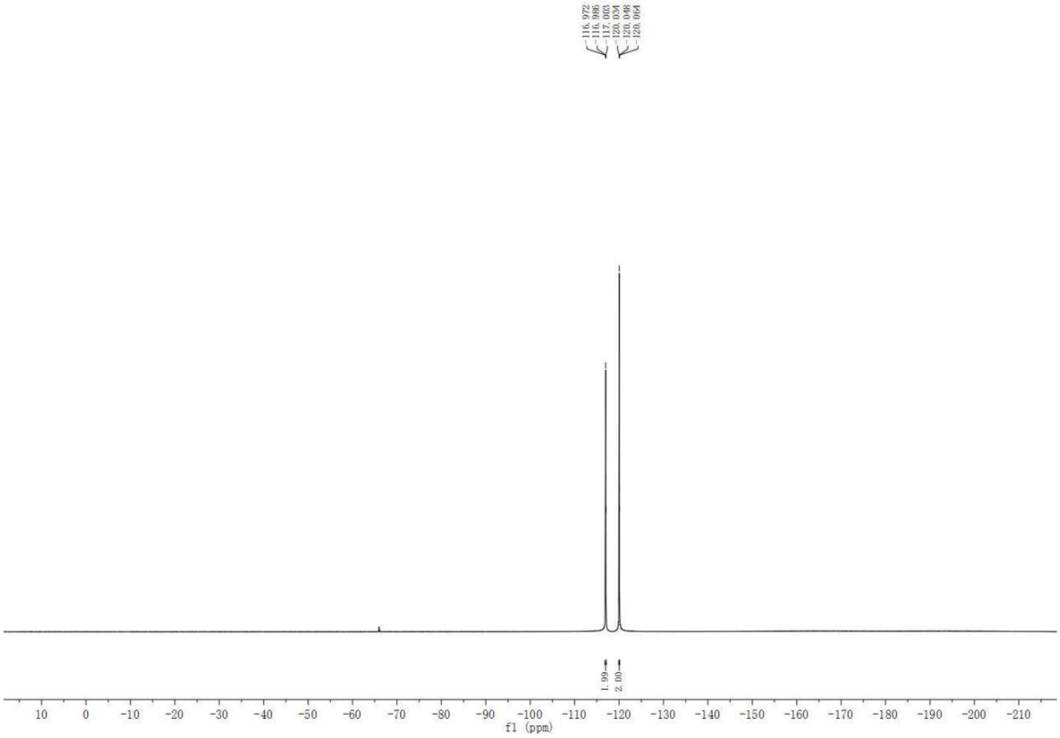

-112.976
-112.990
-113.004
-120.377
-120.391
-120.405
2.01
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

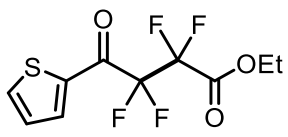

O
F
F
OEt
F
F
O
O

3al

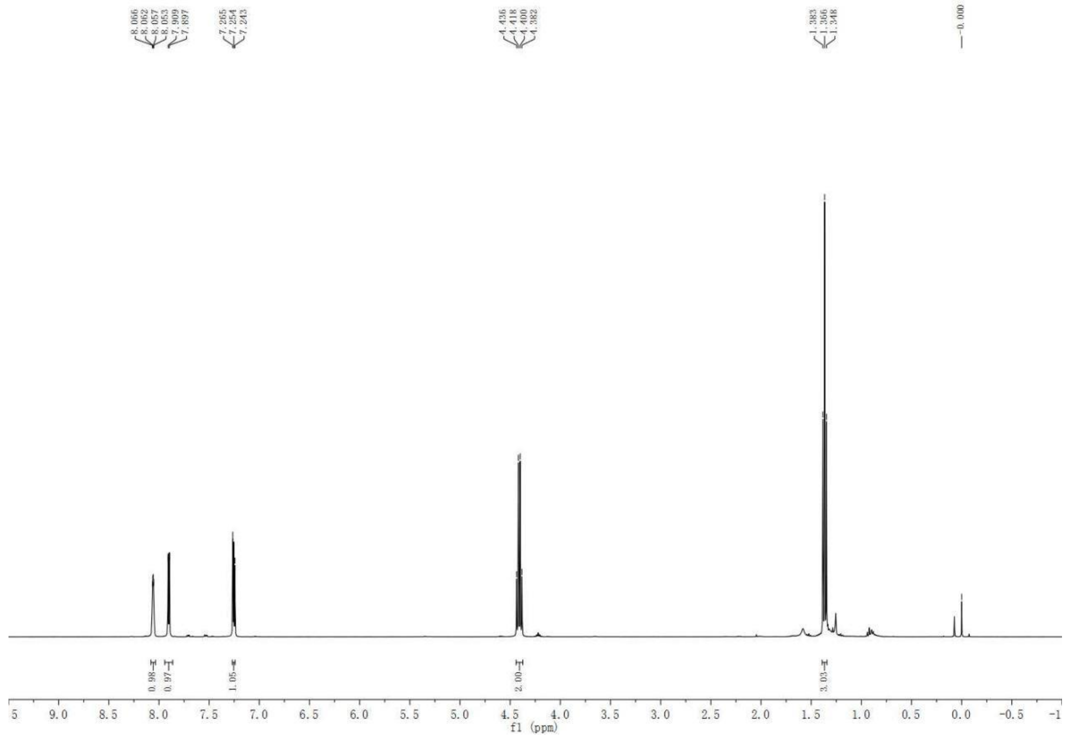

7.825
7.823
7.821
7.819
7.575
7.570
7.564
6.691
6.687
6.681
6.677
4.439
4.421
4.403
4.385
1.388
1.370
1.352
—0.000
0.94
1.00
0.99
2.08
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


151MHz
171.05
171.47
171.28
158.58
158.38
158.19
149.08
146.75
123.70
123.66
123.62
112.22
111.32
111.12
110.92
109.54
109.34
109.14
108.88
108.68
107.57
107.37
107.33
107.13
106.93
105.58
105.38
105.19
76.21
75.99
75.78
63.13
12.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

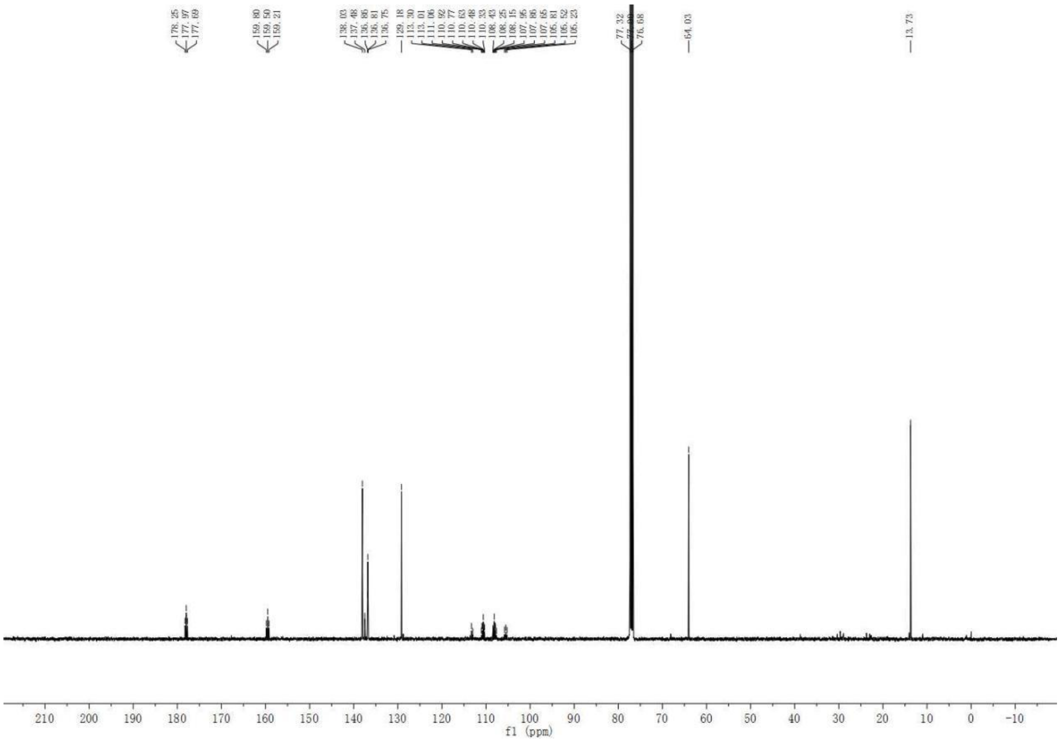

-116.972
-116.986
-117.003
-120.034
-120.048
-120.064
1.99
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



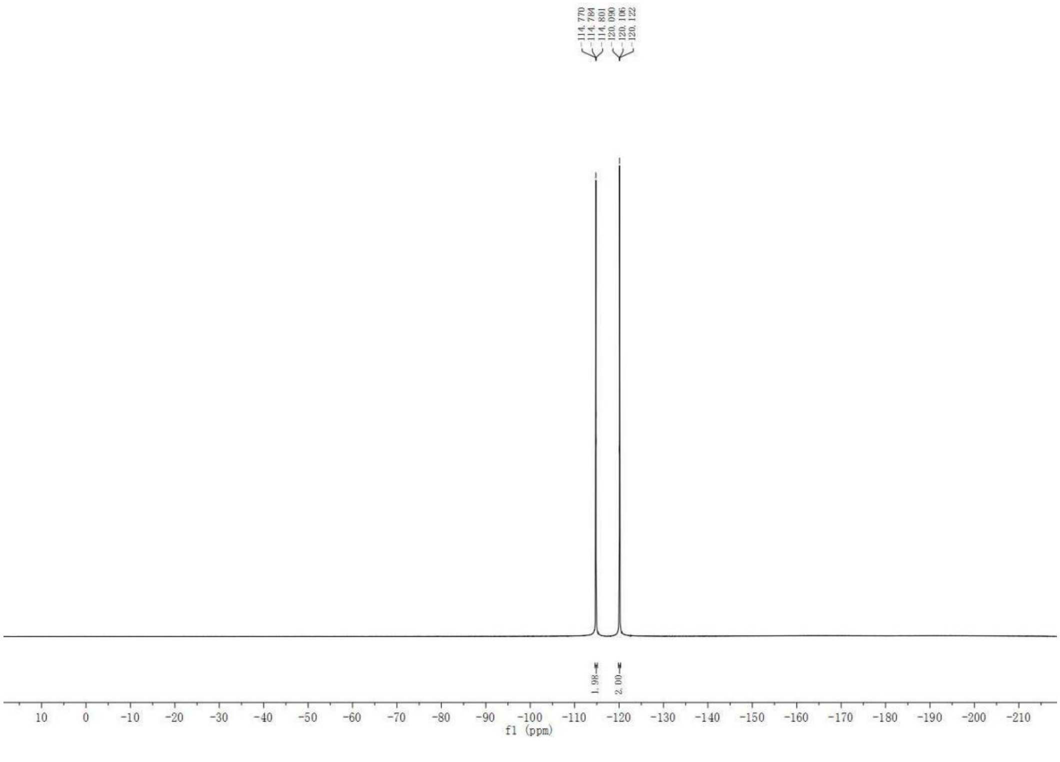
3am

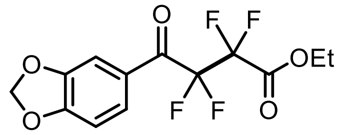


8.066
8.062
8.057
8.053
7.909
7.897
7.255
7.254
7.243
4.436
4.418
4.400
4.382
1.383
1.366
1.348
0.000
0.98
0.97
1.05
2.00
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

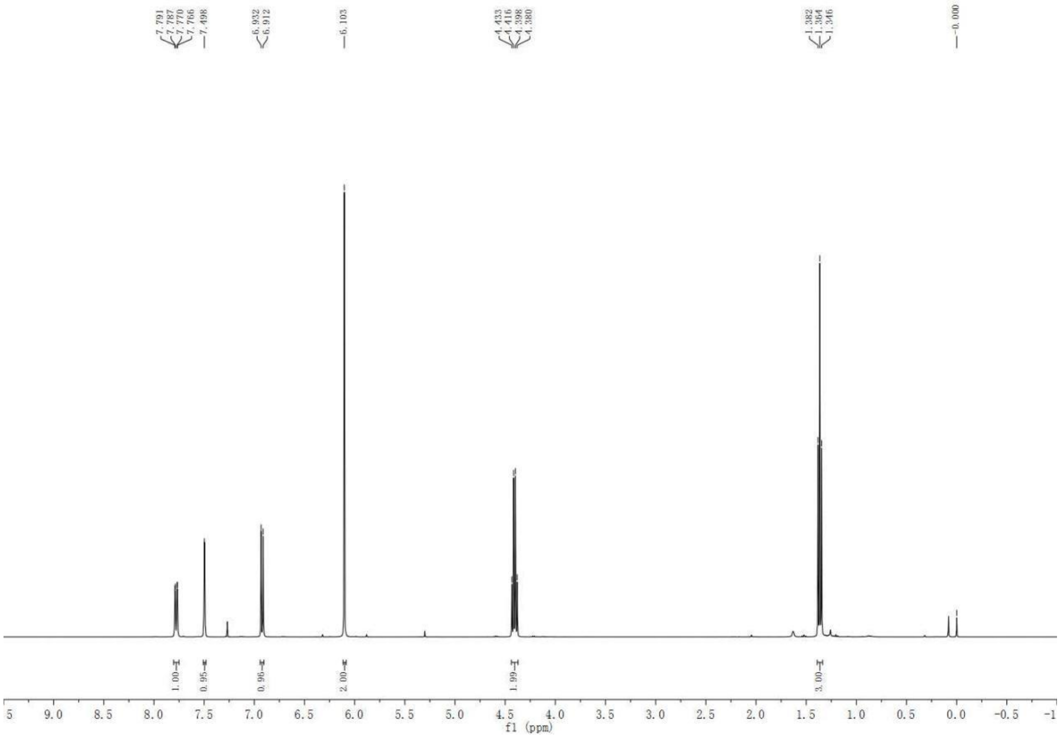


178.25
177.97
177.69
159.80
159.50
159.21
138.03
137.48
136.86
136.81
136.75
129.18
113.30
113.01
111.06
110.92
110.77
110.63
110.48
110.33
108.43
108.25
108.15
107.95
107.86
107.65
105.81
105.52
105.23
77.32
76.68
64.03
13.73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

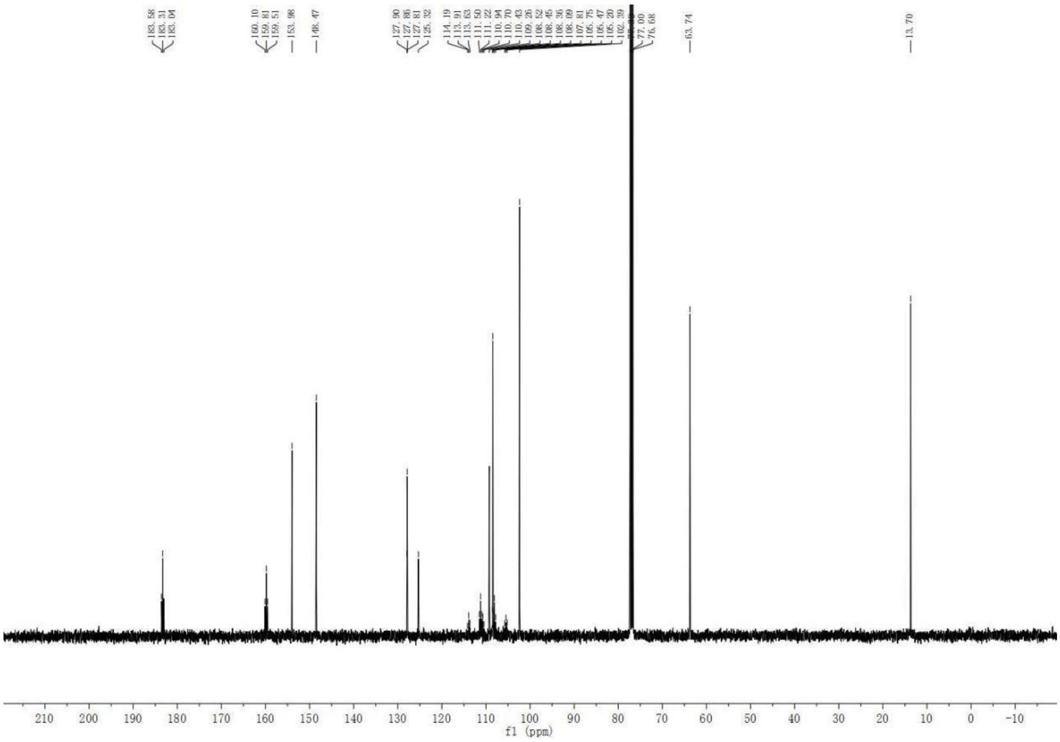

-114.770
-114.784
-114.801
-120.090
-120.106
-120.122
1.98
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

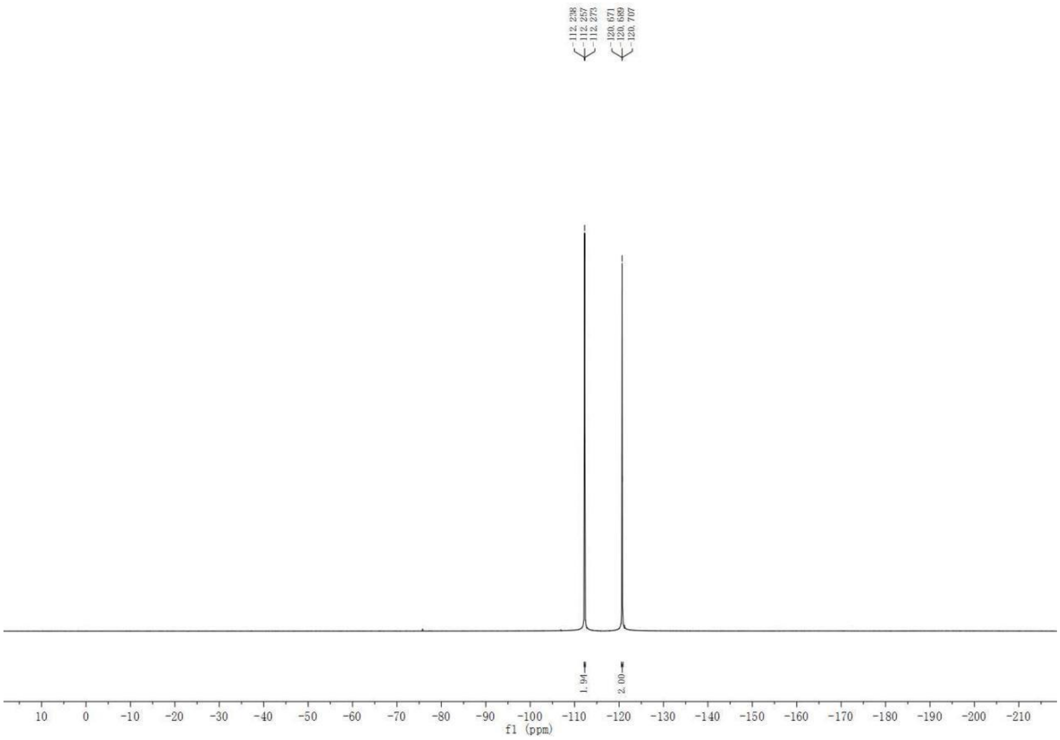


3an

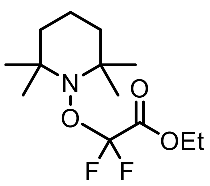


7.791
7.787
7.770
7.766
7.498
6.932
6.912
6.103
4.433
4.416
4.398
4.380
1.382
1.364
1.346
0.000
1.00
0.95
0.96
2.00
1.99
3.00
f1 (ppm)

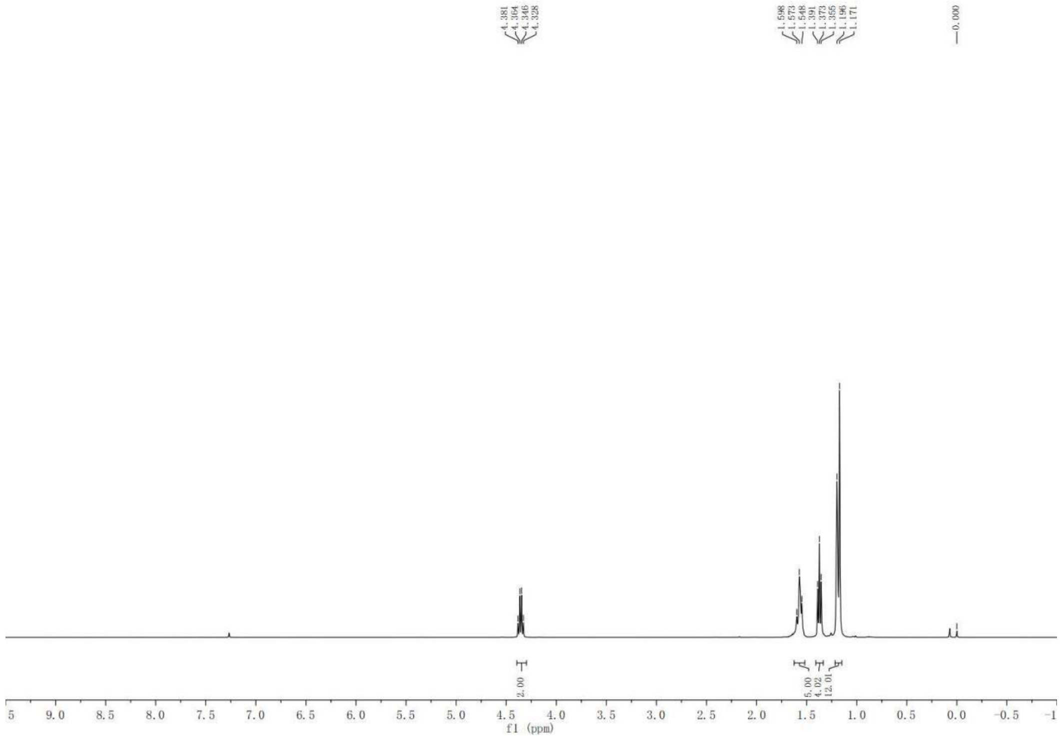

183.58
183.31
183.04
160.10
159.81
159.51
153.98
148.47
127.90
127.86
127.81
125.32
114.19
113.91
113.63
111.50
111.22
110.94
110.70
110.43
109.35
108.52
108.45
108.36
108.09
107.81
105.75
105.47
105.20
102.39
77.00
76.68
63.74
13.70
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

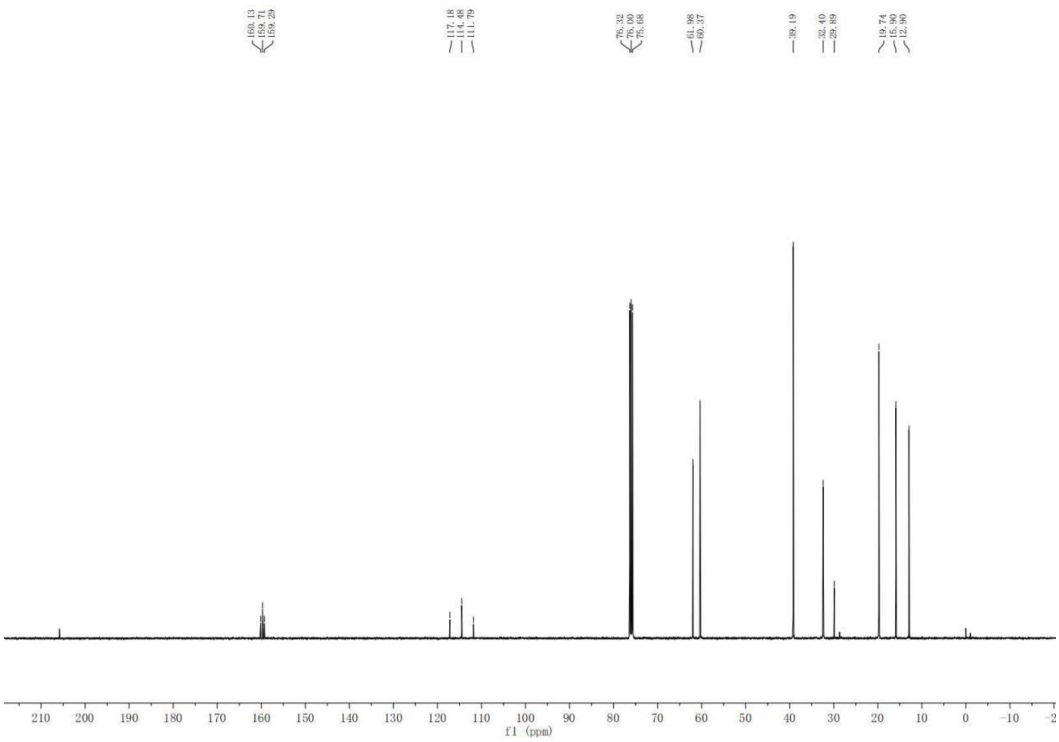


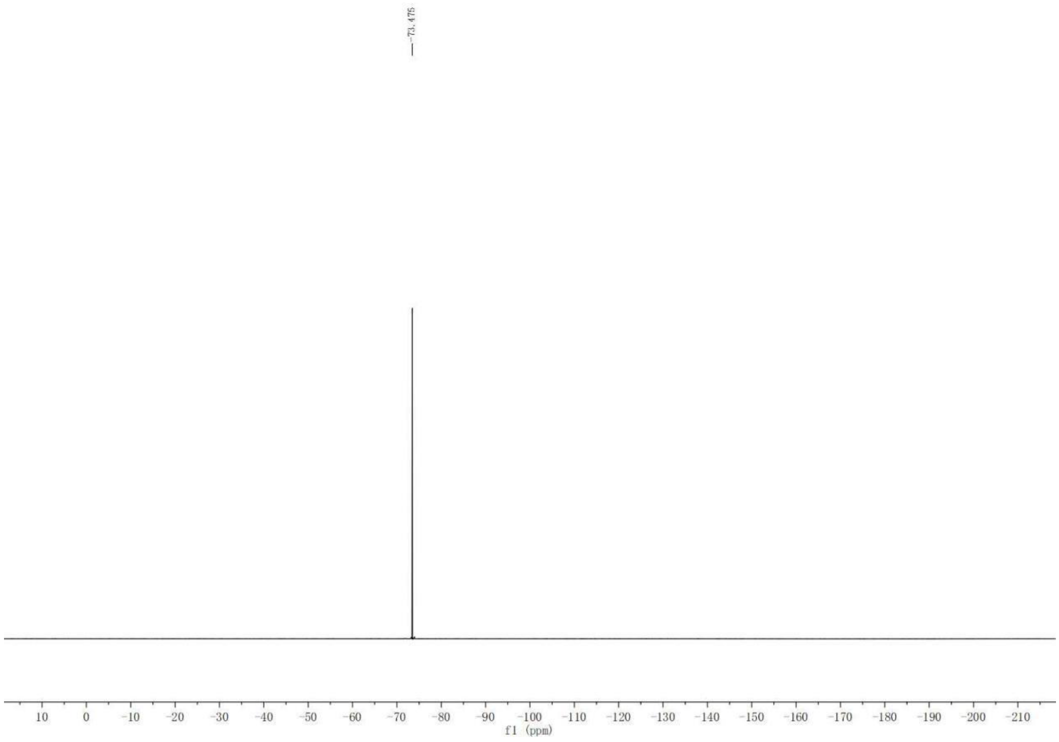
-112.238
-112.257
-112.273
-120.671
-120.689
-120.707
1.94
2.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


N
O
O
OEt
F F

4


4.381
4.364
4.346
4.328
1.598
1.573
1.548
1.391
1.373
1.355
1.196
1.171
0.000
2.00
5.00
4.02
12.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)





-73.475
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)